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(54) 【発明の名称】 インクジェット記録媒体、その製造方法、及びそれを使用した記録物の作成方法

(57) 【要約】

【課題】 本発明は、インクジェット記録方式においてインク吸収性、画像色彩性に優れたインクジェット画像が得られ、屋外などで使用した場合でも耐水性の良い、インクジェット記録物を提供することを目的とするものである。

【解決手段】 支持体上にインク受容層及びその上に主として熱可塑性有機高分子微粒子を含有する層を設け、支持体を介した該インク受容層の反対面に少なくとも1層以上の耐水層が設けられてなるインクジェット記録媒体

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【特許請求の範囲】

【請求項1】 支持体上にインク受容層及びその上に主として熱可塑性有機高分子微粒子を含有する層を設け、支持体のインク受容層を設けてない面に少なくとも1層以上の耐水層が設けられてなるインクジェット記録媒体において、該インク受容層が主として無機微粒子を含有する多孔性層であり、且つ該耐水層が熱可塑性樹脂の溶融押出し法によって設けられたものであることを特徴とするインクジェット記録媒体。

【請求項2】 該インク受容層の無機微粒子が、主としてコロイダルシリカ、アルミナ水和物、γ型酸化アルミニウム、気相法シリカの群から選ばれた少なくとも1種である請求項1記載のインクジェット記録媒体。

【請求項3】 該インク受容層の無機微粒子が、非球状コロイダルシリカ或は擬ベーマイト構造を有するアルミナ水和物である請求項1記載のインクジェット記録媒体。

【請求項4】 該支持体が、坪量120g/m²以上の非塗工紙又は塗工紙である請求項1～3のいずれか一項記載のインクジェット記録媒体。

【請求項5】 該熱可塑性樹脂がポリオレフィン樹脂である請求項1～4のいずれか一項に記載のインクジェット記録用紙。

【請求項6】 該ポリオレフィン樹脂がポリエチレン樹脂或はポリプロピレン樹脂のいずれかである請求項5に記載のインクジェット記録用紙。

【請求項7】 支持体上にインク受容層及びその上に主として熱可塑性有機高分子微粒子を含有する層を設け、支持体を介した該インク受容層の反対面に少なくとも1層以上の耐水層が設けられてなるインクジェット記録媒体の製造方法において、インク受容層とその上に熱可塑性有機高分子微粒子を含有する層を設けた後に、その支持体を介した反対面に熱可塑性樹脂の溶融押出し法によって耐水層を設けることを特徴とするインクジェット記録媒体の製造方法。

【請求項8】 請求項1～7に記載のインクジェット記録媒体に、インクジェット記録後、該熱可塑性有機高分子微粒子を含有する層を溶解または融解して、該熱可塑性有機高分子微粒子が融着した層とすることを特徴とする記録物の作成方法。

【0002】

【従来の技術】インクジェット記録方式は、種々の作動原理によりインクの微小液滴を飛翔させて紙等の記録媒体に付着させ、画像、文字等の記録を行なうものであるが、高速、低騒音、多色化が容易、記録パターンの融通性が高い、現像一定量が不要等の特徴があり、漢字を含め各種図形及びカラー画像等の記録装置として種々の用途において急速に普及している。又、多色インクジェット方式により形成される画像は、製版方式による多色印刷やカラー写真方式による印刷に比較して、遜色のない記録を得ることが可能であるし、更に、作成部数が少なくて済む用途においては、写真技術によるよりも安価であることから、フルカラー画像記録分野にまで広く応用されつつある。

【0003】インクジェット記録方式で使用される記録媒体としては、通常の印刷や筆記に使われる上質紙やコート紙を使うべく、装置やインク組成の面から努力がなされてきた。しかし、装置の高速化・高精細化或はフルカラー化等インクジェット記録装置の性能の向上や用途の拡大に伴い、記録媒体に対してもより高度な特性が要求されるようになった。即ち、当該記録媒体としては、印字ドットの濃度が高く、色調が明るく鮮やかであること、インクの吸収が早くて印字ドットが重なった場合においてもインクが流れ出したり滲んだりしないこと、印字ドットの横方向への拡散が均一で必要以上に大きくなく、且つ周辺が滑らかでぼやけないこと、経時や環境で画質の変化がないこと例えば、耐光性、耐水性、耐オゾン性に優れていること等が要求される。

【0004】このような要求に対して、従来からいくつかの提案が行われてきた。インク吸収性向上や印字ドットの並散防止に対しては支持体上にインク受容層を設ける方法（特開昭52-9074号公報、同58-72495号公報等）、インク受容層中におけるインク中の染料成分の分布状態が色彩性や鮮鋭性に影響することに着目して、染料成分を吸着する特定の剤を用いる方法（特開昭55-144172号公報）等が示されている。又、耐光性、耐水性、耐オゾン性を向上させるために、塩基性オリゴマーを含有させること（特開昭60-11389号公報）、基材中又は基材上の塗工層にポリビニルアミン共重合物を用いること（特開昭64-8085号公報）等が開示されている。

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【0006】しかしながら、これらの特性に対する要求は次第に高度になり、厳しくなる一方で、大判のポスター等に使用される用途においては、これらが屋外で使用され、風雨にさらされたり、直射日光にさらされたりすることも多くなった。従って、これらの環境に対抗できる能力をも保有することが、インクジェット記録媒体に要求される場合もある。

【0007】従来からインクジェット記録方式では、インクとして水性或は油性の溶媒中に染料や顔料を溶解あるいは分散させたインクが使用されてきた。中でも各種の水溶性染料を水または水と有機溶媒との混合物に溶解させた水溶性染料インクが主流である。水溶性染料インクはインクジェット記録装置のインク吐出ヘッドのメンテナンス性に優れており、また、印字後の発色性、解像力等に優れている。しかし、水溶性なるが故に記録画像の耐水性に問題がある。また、水溶性染料は本来耐候性（光や空気、湿度による画像の退色や消失）が劣るため特に記録媒体を屋外展示する場合急速に画像が退色したり、消失したりする欠点がある。

【0008】インクジェット記録媒体の形態としては、所謂、上質紙・ポンド紙等に代表される普通紙タイプと上質紙等の紙、合成紙、合成樹脂フィルム等の支持体表面上にインク受容層を設けた塗工タイプに大別される。塗工タイプのインクジェット記録媒体は、塗設されたインク受容層の種々特性が印字品質に直接影響することから、吸収性に対しては顔料の比表面積や形状の選択、色彩性や色再現性等については顔料の透明性や屈折率の検討、画像品質にたいしては塗層構造や表面形状等、用紙の波打ち等の改善については水中伸度、合成繊維やガラス繊維の配合といった種々の検討、更には塗工方法等について種々検討がなされてきた。

【0009】更にインクジェット記録後に、表面にフィルムを貼り合せたり、クリアな樹脂層を塗工したり、前もってインク受容層表面に熱可塑性有機高分子微粒子の層を設けておき、インクジェット記録後に該熱可塑性有機高分子微粒子を溶融する事によって耐水性や光沢を得ようとする試み（特開昭59-201891号公報、特開昭62-183383号公報、特開平01-182055号公報、特開平01-182081号公報、特開平02-81653号公報、特開平07-237348号公報）もなされている。印字後に熱可塑性有機高分子微

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かの問題があり、更なる改善が求められていた。

【0010】

【発明が解決しようとする課題】本発明は、インクジェット記録方式においてインク吸収性、画像色彩性に優れたインクジェット画像が得られ、屋外などで使用した場合でも耐水性の良い、インクジェット記録物を提供することを目的とするものである。

【0011】

【課題を解決するための手段】本発明者は、前記課題を達成するために鋭意研究した結果、支持体上にインク受容層及びその上に主として熱可塑性有機高分子微粒子を含有する層を設け、支持体のインク受容層を設けてない面に少なくとも1層以上の耐水層が設けられてなるインクジェット記録媒体において、該インク受容層が主として無機微粒子を含有する多孔性層であり、且つ該耐水層を熱可塑性樹脂の溶融押し法によって設けることによって、前記目的を達成できるインクジェット記録物が得られることを見出し本発明を完成するに至った。

【0012】該無機微粒子が主として、コロイダルシリカ、気相法により合成された非晶性シリカ微粒子、アルミナ水和物、γ型酸化アルミニウム微粒子の群から選択された少なくとも1種であるとより好ましい。

【0013】該支持体が、坪量120g/m²以上の非塗工紙又は塗工紙であるとより好ましい。

【0014】該耐水層の熱可塑性樹脂が、ポリオレフィン樹脂であると好ましく、更にポリオレフィン樹脂がポリエチレン樹脂或はポリプロピレン樹脂であるとより好ましい。

【0015】また、支持体上にインク受容層及びその上に主として熱可塑性有機高分子微粒子を含有する層を設け、支持体を介した該インク受容層の反対面に少なくとも1層以上の耐水層が設けられてなるインクジェット記録媒体の製造方法において、インク受容層とその上に熱可塑性有機高分子微粒子を含有する層を設けた後に、その支持体を介した反対面に熱可塑性樹脂の溶融押し法によって耐水層を設けることを特徴とするインクジェット記録媒体の製造方法である。

【0016】更に、上記本発明のインクジェット記録媒体に、インクジェット記録後、該熱可塑性有機高分子微粒子を含有する層を加熱等により、溶解または融解し、

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設けた構成である。

【0018】上記記録媒体の支持体としては、特に制限はなく、一般に用いられている紙や塗工紙が使用できるが、好ましくは、例えば、写真用支持体に用いられているような平滑で密度が高い紙やその上に顔料塗工層を設けた塗工紙である。紙を構成するパルプとしては、天然パルプ、再生パルプ、合成パルプ等を1種もしくは2種以上混合して用いられる。天然パルプとしては、通常製紙用に使用されるパルプ、即ち、針葉樹クラフトパルプ、広葉樹クラフトパルプ、針葉樹サルファイトパルプ、広葉樹サルファイトパルプ等の晒ケミカルパルプ等が、いずれも使用可能である。また、白色度が高いメカニカルパルプであってもよい。更に、藁、エスパルト、バガス、ケナフ等の草類繊維、麻、楮、雁皮、三桠等の樹皮繊維、綿等より製造した非木材パルプでもよい。これらの中では通常工業的に最も多用される針葉樹クラフトパルプ、広葉樹クラフトパルプ、針葉樹サルファイトパルプ、広葉樹サルファイトパルプ等の晒ケミカルパルプが特に好ましい。

【0019】パルプは抄紙適性、ならびに、強度、平滑性、地合の均一性等の紙の諸特性等を向上させるため、ダブルディスクリファイナー等の叩解機により叩解されるのが通常である。叩解の程度は、カナディアンスタンダードフリーネスで通常250m1～450m1の範囲で目的に応じて選択することが出来る。

【0020】叩解されたパルプスラリーは、長網抄紙機、ツインワイヤー抄紙機、または、丸網抄紙機等の抄紙機により抄紙されるが、この際、本発明では、通常抄紙に際して用いられるパルプスラリーの分散助剤、乾燥紙力増強剤、湿潤紙力増強剤、填料、サイズ剤、定着剤等の諸添加物は全て必要に応じて添加することが可能である。更に、必要であればpH調節剤、染料、有色顔料、及び蛍光増白剤等も添加することが可能である。

【0021】分散助剤としては例えばポリエチレンオキサイド、ポリアクリルアミド、とろろあおい等が、紙力増強剤としては例えば植物性ガム、澱粉、カルボキシ変性ポリビニルアルコール等のアニオン性紙力増強剤、カチオン化澱粉、カチオン性ポリアクリルアミド、ポリアミドポリアミンエピクロヒドリン樹脂等のカチオン性紙力増強剤が、填料としては例えばクレー、カオリン、

【0022】また、本発明に用いられる紙支持体は、水溶性高分子添加剤をはじめとする各種の添加剤を含有する液で、タブサイズ、もしくはサイズプレスすることも可能である。

【0023】上記水溶性高分子添加剤としては、例えば澱粉、カチオン化澱粉、酸化澱粉、エーテル化澱粉、リン酸エステル化澱粉等の澱粉誘導体、ポリビニルアルコール、カルボキシ変性ポリビニルアルコール等のポリビニルアルコール誘導体、カルボキシメチルセルロース、ヒドロキシメチルセルロース、ヒドロキシエチルセルロース、セルロースサルフェート等のセルロース誘導体、ゼラチン、カゼイン、大豆蛋白等の水溶性天然高分子、ポリアクリル酸ナトリウム、スチレン-無水マレイン酸共重合体ナトリウム塩、ポリスチレンスルホン酸ナトリウム等、無水マレイン酸樹脂等の水溶性高分子、メラミン樹脂、尿素樹脂等の熱硬化性合成樹脂等の水性高分子接着剤等が用いられ、さらにこの他、サイズ剤として石油樹脂エマルジョン、スチレン-無水マレイン酸共重合体アルキルエステルのアンモニウム塩、アルキルケテンダイマー乳化物、スチレン-ブタジエン共重合体、エチレン-酢酸ビニル共重合体、ポリエチレン、ポリ塩化ビニリデン等のディスパーションが挙げられる。その他の添加剤としては、帯電防止剤として、無機電解質である塩化ナトリウム、塩化カルシウム、ボウ硝等が、吸湿性物質としてグリセリン、ポリエチレングリコール等が、顔料としてクレー、カオリン、タルク、硫酸バリウム、酸化チタン等が、pH調節剤として塩酸、苛性ソーダ、炭酸ソーダ等が用いられ、その他染料、蛍光増白剤、酸化防止剤、紫外線吸収剤等の添加剤を組み合わせて使用することも可能である。

【0024】また、本発明に用いる紙支持体は、抄造中または抄造後、カレンダー等にて圧力を印加して圧縮する等した表面平滑性の良いものが好ましく、JIS-P-8119で測定したベックの平滑度が200秒以上のものが特に好ましい。

【0025】また本発明で使用出来る塗工紙支持体としては、上記紙の上に白色顔料を含有する塗工層を設けたアート紙、コート紙、キャストコート紙、バライタ紙などの塗工紙が挙げられる。

【0026】塗工紙支持体の塗工層に用いられる白色顔

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ト、ポリエチレン、マイクロカプセル、尿素樹脂、メラミン樹脂等の有機顔料等を挙げることができる。中でも、硫酸バリウム、二酸化チタン、酸化亜鉛は高い不透明度と均一な粒子径によって均一な塗工層が形成出来るので好ましい。

【0027】また、支持体の坪量は30～300g/m²程度のものが用いられるが、本発明で好ましく用いられるのは、120g/m²以上の坪量のものである。

【0028】本発明のインクジェット記録媒体における無機微粒子とは、一次粒子径が100nm以下の無機微粒子で、それらが凝集あるいは連結して二次粒子を形成している場合はその平均二次粒子径が20μm以下のものを言う。例えば、非晶性シリカ粒子やアルミナ水和物等が挙げられる。非晶性シリカとしてはいわゆるホワイトカーボン、シリカゲルや微粉末シリカなどである。またアルミナ水和物としては、無定形アルミナゾルや凝ベーマイトなどである。更に言うならば、特開平1-97678号公報、同2-275510号公報、同3-281383号公報、同3-285814号公報、同3-285815号公報、同4-92183号公報、同4-267180号公報、同4-275917号公報などに提案されている凝ベーマイトゾル、特開昭60-219083号公報、同61-19389号公報、同61-188183号公報、同63-178074号公報、特開平5-51470号公報などに記載されているようなコロイダルシリカ、特公平4-19037号公報、特開昭62-286787号公報に記載されているようなシリカ／アルミナハイブリッドゾル、特開平10-119423号公報、特開平10-217601号公報に記載されているような、超微粒子シリカを高遠ホモジナイザーで分散したようなシリカゾル、その他にもヘクタイト、モンモリロナイトなどのスメクタイト粘土（特開平7-81210号公報）、ジルコニアゾル、クロミアゾル、イットリアゾル、セリアゾル、酸化鉄ゾル、ジルコンゾル、酸化アンチモンゾルなどを代表的なものとして挙げることができる。

【0029】本発明のインクジェット記録媒体には、市販の無機微粒子も好適に用いることができる。以下にその一例を挙げるが、本発明はこれに限定されるものではない。例えば、アルミナ水和物としては、カタロイドA

ックスO、スノーテックスC、スノーテックスN、スノーテックス20L、スノーテックスUP、スノーテックスOL、スノーテックスAK、スノーテックスPST-1、スノーテックスK、スノーテックスXS、スノーテックスSS、スノーテックスXL、スノーテックスY、スノーテックスZL、スノーテックスPST-1、スノーテックスPST-3、スノーテックスPST-5、MA-ST、IPA-ST、NBA-ST、IBA-ST、EG-ST、XBA-ST、ETC-ST、D、MAC-ST（以上、日産化学工業製）、カタロイドFS-20L、カタロイドFS-20H、カタロイドFS-30L、カタロイドFS-30H、カタロイドFSI-30、カタロイドFSI-40、カタロイドFSI-50、カタロイドFSI-350、カタロイドFSI-45P、カタロイドFSI-80P、カタロイドSN、カタロイドFSA、カタロイドFSB、USB-1、USB-2、USB-3、OSCAL1132、OSCAL1232、OSCAL1332、OSCAL1432、OSCAL1532、OSCAL1622、OSCAL1722（以上、触媒化成工業製）、シリカ／アルミナハイブリッドゾルとしては、スノーテックスUP-AK1、スノーテックスUP-AK2、スノーテックスUP-AK3（以上、日産化学工業製）、酸化アンチモンゾルとしては、A-1530、A-1550、A-2550（以上、日産化学工業製）、リチウムシリケートとしては、リチウムシリケート35、リチウムシリケート45、リチウムシリケート75（以上、日産化学工業製）などを挙げることができる。

【0030】これらの無機微粒子の中でも特に、コロイダルシリカ、気相法シリカ超微粒子、アルミナ水和物或はγ型酸化アルミニウム微粒子を好適に用いることができる。

【0031】無機微粒子の一つであるコロイダルシリカの形状は、一般的に球状または球状に近い形状をしている。本発明に係わるコロイダルシリカは、小さいシリカ粒子が鎖状に連結した細長い形状、または三次元網目構造を有している非球状のものが好ましい。細長い形状の粒子とは三次元方向には伸長を有さず、同一平面内に伸長したものをいう。細長い形状の粒子には、ほぼ真っ直ぐなもの、屈曲しているもの、分岐を有するもの、端を

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価以上の陽イオンを加えて粒子を成長させることにより得られる。

【0033】ここで活性珪酸とは、珪酸及び粒子径3 nm未満の珪酸の重合体が共存するコロイド粒子であり、公知の方法で容易に得られる。好ましい活性珪酸のコロイド水溶液は、水溶性珪酸塩、例えば $\text{SiO}_2/\text{M}_2\text{O}$ （但し、Mはアルカリ金属原子を示す）モル比が1～4.5程度の水ガラスの希釈液を陽イオン交換処理することにより得られ、 SiO_2 換算で通常6重量%以下、好ましくは1～6重量%含有し、通常pH5以下、好ましくは2～5であるものが用いられる。このpHは、上記水ガラス希釈液を陽イオン交換処理する際、その中の陽イオンの一部分を残存させることによっても、あるいはその中の陽イオンの全部または一部分を除いた後に得られた活性珪酸のコロイド水溶液に少量のアルカリ金属酸化物、水溶性有機塩基等を加えることによっても容易に調整することができる。この活性珪酸のコロイド液は不安定であって、ゲル化しやすい性質を有するので、このゲル化を促進するがごとき不純物となるべく含有しないものが好ましく、また調製直後のものが好ましい。さらに好ましい活性珪酸のコロイド水溶液は、 $\text{SiO}_2/\text{Na}_2\text{O}$ モル比が2～4程度の市販工業製品であるナトリウム水ガラスの希釈水溶液を水蒸気型陽イオン交換樹脂を通過させることにより得られる。

【0034】この活性珪酸のコロイド水溶液に、非球状（鎖状）に連結するように2価以上の陽イオンを加えて粒子を成長させる。2価以上の陽イオンとしては、カルシウムイオン及びマグネシウムイオンが好ましく、カルシウム塩、マグネシウム塩、またはそれらの混合物の形態で、水溶液として添加することが好ましい。このカルシウム塩、マグネシウム塩、またはそれらの混合物の終量としては、上記活性珪酸に対し、それぞれの酸化物として換算した重量比 $[(\text{CaO}+\text{MgO})/\text{SiO}_2]$ では1500～25000ppm、細長い粒子の場合は特に1500～8500ppmとなる量が好ましい。

【0035】また、これらの塩の添加は活性珪酸のコロイド液の攪拌下に行うのが良く、その場合の混合温度及び時間には特に制限はないが、2～50℃で5～30分程度が好ましい。加えられるカルシウム塩及びマグネシウム塩の例としては、カルシウムまたはマグネシウムの

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Sr, Ba, Zn, Sn, Pb, Cu, Fe, Ni, Co, Mn, Al, Cr, Y, 及びTi等の2価、3価または4価の金属が挙げられる。これら多価金属成分の量としては、カルシウム塩及びマグネシウム塩の量をそれぞれ CaO 及び MgO の量に換算した時、これら CaO 及び MgO に対し、多価金属酸化物として10～80重量%程度が好ましい。

【0037】上記水ガラスの希釈液を陽イオン交換処理することによって得られた活性珪酸のコロイド液に上記多価金属分が残留している場合には、この多価金属分は上記10～80重量%の一部として算入する。残部の多価金属分は、上記多価金属の水溶液として、加えられるカルシウム塩及びマグネシウム塩等と一緒に加えるのが好ましい。この多価金属の好ましい例としては、塩化物、硝酸塩、硫酸塩、スルファミン酸塩、硫酸塩、及び酢酸塩等の無機酸塩や有機酸塩が挙げられる。また、亜鉛酸塩、錳酸塩、アルミン酸塩、及び鉛酸塩等、例えば、アルミン酸ナトリウム、錳酸ナトリウム等の塩も用いることができる。加えられる上記カルシウム塩、マグネシウム塩、及び多価金属塩等は、活性珪酸のコロイド液と均一に混合するのが好ましく、通常、水溶液として添加される。

【0038】上記の工程によって得られた水性液に、アルカリ金属水酸化物、水溶性有機塩基、またはそれらの水溶性珪酸塩を加える。この添加は、上記工程の終了後なるべく早く、そして攪拌下に行うのが好ましい。またこれらの混合の温度及び時間には特に制限はないが、2～50℃で5～30分程度が好ましい。加えられるアルカリ金属水酸化物、水溶性有機塩基、またはそれらの水溶性珪酸塩は、上記工程によって得られた水性液と均一に混合されるのが好ましく、直接または水溶液として添加される。

【0039】アルカリ金属水酸化物としては、例えば、ナトリウム、カリウム、及びリチウム等の水酸化物が挙げられる。有機塩基としては、例えば、テトラエタノールアンモニウム水酸化物、モノメチルトリエタノールアンモニウム水酸化物、テトラメチルアンモニウム水酸化物等の第4級アンモニウム水酸化物類、モノエタノールアミン、ジエタノールアミン、トリエタノールアミン、N, N-ジメチルエタノールアミン、N-(β-アミノ

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上記アルカリ金属水酸化物のアルカリ金属原子または有機塩基の分子をMで表せば、加えられるアルカリ金属水酸化物、有機塩基またはそれらの水溶性珪酸塩の量は、活性珪酸に由来するシリカ分及び珪酸塩のシリカ分の合計を SiO_2 として、 SiO_2/M_2O が20～200、好ましくは60～100のモル比となる量が良い。この添加によって、液はpH7～10程度を示すに至る。

【0041】以上の工程により得られた混合物を60～300℃で30分～40時間、好ましくは90～150℃で2～12時間加熱することにより SiO_2 濃度1～6重量%の非球状の形状を有するシリカゾルが得られる。所望によりこのゾルを濃縮することにより、より高濃度なゾルが得られる。尚、上記の方法によって得られた非球状のシリカ粒子は、動的光散乱法により測定した二次粒子径が40～300nmの範囲であり、電子顕微鏡観察によると5～40nmの太さで一平面内または三次元的に成長した形状を有している。

【0042】本発明に係わる非球状のシリカ粒子は、少なくとも本発明のインクジェット記録媒体におけるインク受容層を形成するための塗液において、非球状の形状で存在していれば良く、インク受容層形成用塗液の調液に先だって、上記の方法を含めて本発明に係わる非球状のシリカ粒子を調製し、これを用いてインク受容層形成用塗液を調製しても良いし、インク受容層形成用塗液調液時に、塗液中で上記の方法を含めて本発明に係わる非球状のシリカ粒子を調製しつつ塗液を調液しても良い。塗液調液前に予め本発明に係わる非球状のシリカ粒子を用意しておくのであれば、市販のものも用いることができる。市販の非球状のシリカ粒子の例としては、日産化学工業製スノーテックスUP、及びスノーテックスOU

P等が挙げられる。

【0043】コロイダルシリカ以外のシリカ微粒子は、いわゆるホワイトカーボン、シリカゲルや微粉末シリカなどの非晶性シリカがある。非晶質シリカ微粒子の製造方法としては、液相法、粉碎固相法、晶析固相法および気相法がある。液相法とは、いわゆる液中に存在する珪酸化合物等を、化学変化または物理変化によって固体状態に析出させる微粒子製造方法である。粉碎固相法とはシリカ固体を機械的に粉碎する方法であり、晶析固相法とは溶融や固体の相転移などを利用した微粒子製造方法

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より合成された非晶性シリカ微粒子として市販されている製品としては、アエロジル（デグサ社）が該当する。

【0045】本発明で使用する気相法シリカ微粒子ゾルは、上記の一次粒子径をもつシリカ微粒子を水に添加し、高速ホモジナイザー等で分散して平均二次粒子径が200nm以下、好ましくは100nm以下にまで分散したものである。

【0046】本発明に用いられるアルミナ水和物は、下記の一般式により表すことができる。



アルミナ水和物は組成や結晶形態の違いにより、ジブサイト、バイアライト、ノルストランドイト、ペーマイト、ペーマイトゲル（擬ペーマイト）、ジアスポア、無定形非晶質等に分類される。中でも、上記の式中、nの値が1である場合はペーマイト構造のアルミナ水和物を表し、nが1を越え3未満である場合は擬ペーマイト構造のアルミナ水和物を表し、nが3以上では非晶質構造のアルミナ水和物を表す。特に、本発明に好ましいアルミナ水和物は、少なくともnが1を越え3未満の擬ペーマイト構造のアルミナ水和物である。

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【0047】アルミナ水和物が十分なインク吸収速度を有するには、アルミナ水和物の平均細孔半径が1乃至10nmであることが好ましく、特に、3乃至7nmであることが好ましい。細孔半径が小さすぎるとインクの吸収が困難となり、細孔半径が大きすぎると、インク中の染料の定着が悪くなり画像のぼれが発生する。

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【0048】アルミナ水和物が十分なインク吸収容量を有するには、アルミナ水和物の細孔容積が0.3乃至0.8ml/gの範囲であることが好ましく、特に、0.4乃至0.6ml/gの範囲であることが好ましい。インク受容層の細孔容積が大きい場合にはインク受容層にひび割れや粉落ちが発生し、細孔容積が小さい場合にはインクの吸収が遅くなる。更に、単位面積当たりのインク受容層の溶媒吸収量は5ml/m²以上、特に10ml/m²以上であることが好ましい。単位面積当たりの溶媒吸収量が小さい場合には、特に多色印刷を実施した場合にインクが溢れることがある。

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【0049】アルミナ水和物がインク中の染料を十分に吸収し、定着するにはBET比表面積が70乃至300m²/gの範囲であることが好ましい。BET比表面積

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の比で表される。ここで粒子の直径とは、アルミナ水和物を電子顕微鏡で観察したときの粒子の投影面積に等しい円の直径を表す。アスペクト比が上記の範囲より小さい場合は、インク受容層の細孔径分布が狭くなり、インク吸収性が低下する。一方アスペクト比が上記の範囲を超える場合は、粒子を揃えてアルミナ水和物を製造することが困難となる。

【0051】本発明に用いられるアルミナ水和物は、アルミニウムイソプロポキシド等のアルミニウムアルコキシドの加水分解、アルミニウム塩のアルカリによる中和、アルミン酸塩の加水分解等公知の方法によって製造することができる。また、アルミナ水和物の粒子径、細孔径、細孔容積、比表面積等の物性は、析出温度、熟成温度、熟成時間、液のpH、液の濃度、共存化合物等の条件によって制御することができる。

【0052】アルコキシドからアルミナ水和物を得る方法としては、特開昭57-88074号公報、同62-56321号公報、特開平4-275917号公報、同6-64918号公報、同7-10535号公報、同7-267633号公報、米国特許第2,656,321号明細書等にアルミニウムアルコキシドを加水分解する方法として開示されている。これらのアルミニウムアルコキシドとしてはイソプロポキシド、2-ブトキシド等が挙げられる。

【0053】また、特開昭54-116398号公報、同55-23034号公報、同55-27824号公報、同56-120508号公報には、アルミニウムの無機塩またはその水和物を原料として使用する方法が開示されている。原料としては、例えば塩化アルミニウム、硝酸アルミニウム、硫酸アルミニウム、ポリ塩化アルミニウム、アンモニウムミョウバン、アルミン酸ナトリウム、アルミン酸カリウム、水酸化アルミニウム等の無機塩およびその水和物を挙げることができる。

【0054】更に別の方法として、特開昭56-120508号公報に記載されている如き、pHを酸性側乃至塩基性側に交互に変動させ、アルミナ水和物の結晶を成長させる方法、特公平4-33728号公報に記載されている如き、アルミニウムの無機塩から得られるアルミナ水和物と、バイヤー法で得られるアルミナとを混合し、アルミナを再水和する方法もある。

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結晶微粒子を使用すると、インク受容層の印字性、吸収性は良好であるものの、透明性に欠け、塗膜欠陥が発生しやすくなる。一次粒子の平均粒子径は、80nm未満であることが好ましい。80nm以上の一次粒子からなる2次粒子を使用すると、脆弱性が増し、塗膜欠陥が非常に発生しやすくなる。

【0057】 γ 型アルミナ結晶微粒子ゾルを得るには、通常、数千から数万nmの2次粒子となっている γ 型アルミナ結晶をビーズミルや超音波ホモジナイザー、高圧式ホモジナイザー等の粉碎手段によって、平均粒子径が200nm以下、好ましくは100nm以下の超微粒子になるまで粉碎する。平均粒子径が200nmを超えると、インク吸収性は増加するが、被膜が脆く、透明性が低下する。粉碎手段としては、超音波ホモジナイザーや高圧式ホモジナイザーを用いる方法が好ましく、ビーズミル等の他の粉碎方法では、 γ 型アルミナ結晶が硬い結晶であるために、粉碎容器から異物が混入しやすく、透明性の低下や欠陥の発生の原因となる。 γ 型アルミナ結晶微粒子は、インク吸収性に優れ、乾燥性、インク定着性等の印字品質もよく、超微粒子化することで、高比率でインク受容層に含有させても透明性に優れたインクジェット記録媒体を得ることができる。

【0058】 γ 型アルミナ結晶微粒子は、市販品として、 δ グループに属する酸化アルミニウムC（日本アエロジル（株）製）、 γ グループに属するAKP-G015（住友化学（株）製）などとして入手できる。

【0059】本発明に用いられる無機微粒子のバインダーとして、水溶性あるいは非水溶性の高分子化合物を添加しても良い。本発明に用いられる高分子化合物は、インク受容層の構成成分として、インクと親和性を有する化合物である。例えば、水溶性高分子化合物としてはポリビニルアルコール、アクリル樹脂、スチレン-アクリル共重合体、無水マレイン酸重合体、スチレン-無水マレイン酸共重合体、エチレン-酢酸ビニル共重合体、でんぷん、ポリビニルブチラール、ゼラチン、カゼイン、アイオノマー、アラビアゴム、カルボキシメチルセルロース、アルギン酸、アルギン酸ナトリウム、プルラン、ポリビニルピロリドン、ポリアクリルアミド、ポリエチレングリコール、ポリプロピレングリコール等である。

好ましくは、ポリビニルアルコールである。

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できる為、特に好ましい。

【0061】これらの高分子化合物は、単独乃至複数を併用してもよく、無機微粒子に対し、2～30重量%を添加する。好ましくは、5～20重量%を添加する。上記の添加量の範囲以下では塗膜強度が弱くなり、多すぎるとインク吸収性が低下する。

【0062】本発明において、インク受容層の層構成は、単層であっても積層構成であってもよい。積層構成の場合、全層が同じ配合の層であってもよいし、他の成分で構成される層との積層構成であってもよい。

【0063】本発明の無機微粒子を含有するインク受容層の塗工量は、固形分換算で単位平方メートル当たり5g以上が必要であり、本発明のさなる効果を確認するには、好ましくは単位平方メートル当たり12g以上60g以下である。

【0064】更に、本発明の無機微粒子と必要ならバインダーとを含有するインク受容層を形成する塗工液は、必要に応じて、界面活性剤、無機顔料、着色染料、着色顔料、インク染料定着剤（カチオン性樹脂）、紫外線吸収剤、酸化防止剤、顔料の分散剤、消泡剤、レベリング剤、防曇剤、蛍光増白剤、粘度安定剤、pH調整剤、硬膜剤等の公知の各種添加剤を添加することができる。

【0065】本発明で使用出来る熱可塑性有機高分子微粒子としては、例えばポリスチレン、ポリメチルスチレン、ポリメトキシスチレン、ポリクロルスチレン等のポリモノビニリデン芳香族、ポリ塩化ビニル、ポリビニルシクロヘキサン、ポリエチレン、ポリプロピレン、ポリ塩化ビニリデン等のポリオレフィン及びポリハロオレフィン類、ポリメタクリレート、ポリクロルアクリレート、ポリメチルメタクリレート等の α 、 β -エチレン性不飽和酸のエステル類の重合体等及びこれらの共重合体等が挙げられる。特に低密度ポリオレフィンは好ましく使用出来る。

【0066】熱可塑性有機高分子微粒子は、例えば一種またはそれ以上のビニル単量体からエマルジョン重合してつくった、スラリー状のプラスチックピグメントやラテックス、及びその乾燥物や固体状のプラスチックを各種手段によって粉碎した微粉末や微粒状に成型した粉末等として得られる。これら熱可塑性有機高分子微粒子の大きさとしては通常直径0.01 μ m～50 μ mのもの

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することにより、熱可塑性有機高分子微粒子皮膜の粘着性を弱めることができ、加熱皮膜化する際に加熱ロールに粘着することがなくなるので好ましい。30部以上加えると皮膜の連続性を阻害し、画像の耐水性を低下させることがある。

【0068】本発明で用いられる熱可塑性有機高分子微粒子を含む塗工層に含有されるコロイダルシリカとしては、例えば粒子径5nm以上100nm以下の球状コロイダルシリカや、これらが複数個結合して30nm以上800nm以下の粒子径を有する非球状コロイダルシリカ等が挙げられる。

【0069】本発明に用いられる熱可塑性有機高分子微粒子を含む塗工層には、バインダーとして高分子化合物を含んでもよい。好ましい高分子化合物としては、例えば、ポリビニルアルコール、アクリル樹脂、スチレン-アクリル共重合体、無水マレイン酸重合体、スチレン-無水マレイン酸共重合体、エチレン-酢酸ビニル共重合体、でんぷん、ポリビニルピリジン、ゼラチン、カゼイン、アイオノマー、アラビアゴム、カルボキシメチルセルロース、アルギン酸、アルギン酸ナトリウム、プルラン、ポリビニルピロリドン、ポリアクリルアミド、ポリエチレングリコール、ポリプロピレングリコール等である。また、非水溶性の高分子化合物としては、例えば、ポリ酢酸ビニルなどのポリビニルエステル類、ブチラール樹脂などのポリアセタール類、ポリアクリル酸エチルなどのポリアクリル酸エステル類等のラテックス類である。好ましくは、エチレン-酢酸ビニル共重合体エマルジョンやポリビニルピロリドンである。これらの高分子化合物は、単独乃至複数を併用してもよく、熱可塑性有機高分子微粒子に対し、1～30重量%を添加する。好ましくは、3～20重量%である。上記の添加量の範囲以下では熱可塑性有機高分子微粒子の接着性が不良になり、添加量の範囲以上ではインク吸収性を阻害する。

【0070】最表層の裏面的に熱可塑性有機高分子微粒子とバインダーからなる層は塗工量（乾燥固形分）として、0.5g/m²～50g/m²が好ましい。更に、その他の添加剤として、顔料分散剤、増粘剤、流動性改良剤、消泡剤、抑泡剤、離型剤、発泡剤、浸透剤、着色染料、着色顔料、蛍光増白剤、紫外線吸収剤、酸化防止剤、防曇剤、防バイ剤、染料定着剤（カチオン性高

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することができる。

【0073】塗工後に乾燥する手段としては、一般の公知の方法を用いることができ、限定されない。例えば、熱源により発生した加熱空気を送風した加温器内に搬送する方法、ヒーター等の熱源近傍を通過させる方法等である。最表層の熱可塑性高分子微粒子が溶融しない温度で乾燥できれば、どんな方法でもよい。

【0074】又、塗工後には、マシンカレンダー、スーパーカレンダー、ソフトカレンダー等のカレンダーを用いて仕上げて良い。

【0075】本発明における熱可塑性有機高分子微粒子からなる最表層の役割は、飛翔し最表層に付着したインクを、直ちに吸収し溶媒を下層に受け渡すことと、インクジェット記録後、適当な手段によって被膜化し、記録画像を水や光から保護する層となることである。

【0076】本発明のインク受容層と熱可塑性有機高分子微粒子層のある支持体を介した反対側には、熱可塑性樹脂を溶融押出し法によって塗工した耐水層を設ける。

【0077】熱可塑性樹脂としては、ポリオレフィン樹脂やポリエステル樹脂が挙げられる。ポリオレフィン樹脂としては、低密度ポリエチレン、高密度ポリエチレン、ポリプロピレン、ポリブテン、ポリペンテンなどのオレフィンのホモポリマーまたはエチレン-プロピレン共重合体などのオレフィンの2つ以上からなる共重合体およびこれらの混合物である。ポリエステル樹脂としては、ポリエチレンテレフタレート、ポリブチレンテレフタレートやポリエチレンナフタレート等である。これらの熱可塑性樹脂は、各種の密度、溶融粘度指数（メルトインデックス）のものを単独にあるいはそれらを混合して使用できる。好ましくは、ポリエチレン樹脂、ポリプロピレン樹脂である。

【0078】また、該熱可塑性樹脂中には、酸化チタン、酸化亜鉛、タルク、炭酸カルシウムなどの白色顔料、ステアリン酸アミド、アラキジン酸アミドなどの脂肪酸アミド、ステアリン酸亜鉛、ステアリン酸カルシウム、ステアリン酸アルミニウム、ステアリン酸マグネシウムなどの脂肪酸金属塩、コバルトブルー、群青、セシリアンブルー、フタロシアニンブルーなどのブルーの顔料や染料、コバルトバイオレット、ファストバイオレット、マンガン紫などのマゼンタの顔料や染料、電光線白

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ないが、微粗面表面のクーリングロールを使用して、光沢をやや抑えた表面がよく使用される。

【0080】また、耐水層の塗工はインク受容層や熱可塑性有機高分子微粒子層を設ける前に塗工してあってもかまわないが、好ましくはインク受容層や熱可塑性有機高分子微粒子層を塗工してから、最後に耐水層を設けるのがよい。その理由は、支持体に前もって耐水層があると熱可塑性有機高分子微粒子層がきれいに塗工出来ず、面が荒れることがあるからである。耐水層は熱可塑性樹脂を加熱溶融して押出しコーティング法によって設ける訳であるが、通常加熱溶融温度は300℃前後の高い温度が使われている。インク受容層の表面に設けた熱可塑性有機高分子微粒子層の該熱可塑性有機高分子微粒子の可塑化温度は50℃～150℃程度であるが、その層を設けてからその反対面に300℃に加熱溶融した樹脂を塗設して耐水層を設けても、なんら熱可塑性有機高分子微粒子層に影響することなく耐水層が塗設できる。それは加熱溶融樹脂が紙に塗設直後にクーリングロールで冷やされるため、紙支持体を介して反対側にある該熱可塑性有機高分子微粒子層にまで、熱が及ばない為である。

【0081】更にその耐水層の上には、帯電防止性、搬送性、カール防止性、筆記性、糊付け性等のために、各種のオーバー層を塗設することができる。オーバー層には、無機帯電防止剤、有機帯電防止剤、親水性バインダー、ラテックス、硬化剤、顔料、滑剤、マット化剤、界面活性剤等を適宜組み合わせることで添加せしめることが出来る。

【0082】本発明のインクジェット記録媒体は、インクジェット記録装置で文字や画像を記録したままの状態では、熱可塑性有機高分子微粒子層が空隙を有しているために、画像は白っぽく、あまり鮮明ではない。本発明ではインクジェット記録画像を記録した後、最表層の熱可塑性有機高分子微粒子を、溶解、又は融解して被膜化して耐水性の透明な層に変化させる工程が必要である。

【0083】最表層を被膜化する方法としては、熱可塑性有機高分子の溶媒を付与して溶解させたり、熱を加えて融解被膜化する方法等がある。熱を加えるに際して熱可塑性有機高分子の軟化点を下げる物質、特に可塑剤を

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又、実施例において示す「部」及び「%」は、特に明示しない限り重量部及び重量%を示す。

【0086】＜支持体Aの作製＞ダブルディスクリファイナーで320ml、csfまで叩解した広葉樹漂白クラフトパルプを75重量%、及びダブルディスクリファイナーで430ml、csfまで叩解した針葉樹漂白クラフトパルプを25重量%から成る混合パルプに対し、カチオン化澱粉1.0重量%、アルキルケテンダイマーサイズ剤0.1重量%、及び重質炭酸カルシウム填料を7重量%添加して紙料スラリーを調製した。その紙料スラリーから、長網抄紙機で紙匹を形成しプレスで搾水後、多筒式ドライヤー乾燥工程で乾燥し、乾燥の途中で酸化澱粉の5重量%溶液をサイズプレスし（付着量は両面乾燥固形分で3.5g/m²）、最終的に得られる基紙水分が絶乾水分で8重量%になるように乾燥し、マシンカレンダー処理して、坪量120g/m²のインクジェット記録媒体用の支持体Aを製造した。

【0087】＜支持体Bの作製＞上記支持体Aのインク受容層を設ける側に、白色顔料として硫酸バリウム（バライタ）100部、接着剤としてポリビニルアルコール10部からなる塗工液を乾燥固形分で10g/m²になるように塗工乾燥して、支持体Bを製造した。

【0088】＜アルミナ水和物の合成＞イオン交換水1200g、イソプロピルアルコール900gを3Lの反応器に仕込み、75℃に加熱した。アルミニウムイソプロポキシド408gを加え、75℃で24時間、続き95℃で10時間加水分解を行った。加水分解後、酢酸24g加えて95℃で48時間攪拌した。次に、固形分濃度が15重量%になるように濃縮し、白色のアルミナ水和物の分散液を得た。このゾルを室温で乾燥させ、X線回折を測定したところ、擬ベーマイト構造を示した。また、透過型電子顕微鏡で平均粒径を測定したところ、30nmであり、アスペクト比6.0の平板状のアルミナ水和物であった。また、窒素吸着脱着方法によって平均細孔半径、細孔容積およびBET比表面積を測定したところ、それぞれ7.1nm、0.65ml/gそして200m²/gであった。

【0089】＜インク受容層塗工液A＞前記の15重量%のアルミナ水和物の分散液を用いて、アルミナ水和物分散液100部に対し、10重量%のポリビニルアルコ

*液を15部混合した。混合後、ホモミキサーに1万rpmで10分間かけ、均一分散化した。分散液は、所定の濃度になるようにエバポレータにより濃縮化し、塗工液Bとした。

【0091】＜インク受容層塗工液C＞アルミナ微粒子として、δグループのγ型アルミナ結晶粉末である、一次粒子径13nmのアエロジル酸化アルミニウムC（日本アエロジル社製）600gを2400gのイオン交換水中に攪拌機にて分散し、20重量%のスラリー状の粘性液を調製した。この20重量%のγ型アルミナ分散液を用いて、アルミナ分散液100部に対し、10重量%のポリビニルアルコール（クラレ社製PVA235）水溶液を30部混合した。混合後、ホモミキサーに1万rpmで10分間かけ、均一分散化した。分散液は、所定の濃度になるようにエバポレータにより濃縮化し、塗工液Cとした。

【0092】＜インク受容層塗工液D＞インク受容層の塗被組成物は、一次粒子径7nmの気相法微粒子シリカ（AEROSIL300：日本アエロジル社製）100gを、500gのイオン交換水中に攪拌機にて分散し、10重量%のポリビニルアルコール（クラレ社製PVA235）水溶液を80gを混合し、塗工液Dとした。

【0093】＜インク受容層塗工液E＞インク受容層の塗被組成物は、市販の球状コロイダルシリカとして、スノーテックスO（日産化学工業社製、一次粒子径10～20nm、SiO₂濃度20～21重量%）200部、10重量%のポリビニルアルコール（クラレ社製PVA117）30部、カチオン性染料定着剤（スミレッズレジン1001：住友化学社製）20部を混合し、塗工液Eとした。

【0094】＜インク受容層塗工液F＞インク受容層の塗被組成物は、市販の非球状コロイダルシリカとして、スノーテックスUP（日産化学工業社製、一次粒子径10～20nm、平均二次粒子径約70nm、SiO₂濃度20～21重量%）200部、10重量%のポリビニルアルコール（クラレ社製PVA117）30部、カチオン性染料定着剤（スミレッズレジン1001：住友化学社製）20部を混合し、塗工液Fとした。

【0095】＜インク受容層塗工液G＞インク受容層の塗被組成物は、一次粒子径約10～30nm、平均二次

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(固形分)

ポリビニルピロリドン

3. 0部

【0097】

<熱可塑性有機高分子微粒子含有層配合B>

熱可塑性有機高分子微粒子(ケミパールM200:三井化学社製) 25部

(固形分)

コロイダルシリカ(スノーテックスO、日産化学社製)

7部

ポリビニルピロリドン

3. 0部

【0098】実施例1

支持体Aに、インク受容層配合Aの塗工液をカーテンコーターにより乾燥塗工量15g/m²になるように塗工、乾燥し、その上に熱可塑性有機高分子微粒子含有層配合Aの塗工液をカーテンコーターにより乾燥塗工量10g/m²になるように塗工、乾燥した。次いで密度0.962g/cm³の高密度ポリエチレン樹脂を320℃で熔融し、支持体のインク受容層を設けてない面に厚さ30μmになるように押出コーティングし、粗面クーリングロールを用いて光沢度5%の裏面樹脂被覆をして耐水層を作成し、実施例1のインクジェット記録媒体を作製した。

【0099】実施例2

支持体Aに、インク受容層配合Aの塗工液をカーテンコーターにより乾燥塗工量15g/m²になるように塗工、乾燥し、その上に熱可塑性有機高分子微粒子含有層配合Bの塗工液をカーテンコーターにより乾燥塗工量10g/m²になるように塗工、乾燥した。次いで密度0.962g/cm³の高密度ポリエチレン樹脂を320℃で熔融し、支持体のインク受容層を設けてない面に厚さ30μmになるように押出コーティングし、粗面クーリングロールを用いて光沢度5%の裏面樹脂被覆をして耐水層を作成し、実施例2のインクジェット記録媒体を作製した。

【0100】実施例3

実施例1において、インク受容層配合Aに替えてインク受容層配合Bを使用した他は、実施例1と同様にして実施例3のインクジェット記録媒体を作製した。

【0101】実施例4

実施例2において、インク受容層配合Aに替えてインク受容層配合Bを使用した他は、実施例2と同様にして実施例4のインクジェット記録媒体を作製した。

受容層配合Dを使用した他は、実施例1と同様にして実施例7のインクジェット記録媒体を作製した。

【0105】実施例8

実施例2において、インク受容層配合Aに替えてインク受容層配合Dを使用した他は、実施例2と同様にして実施例8のインクジェット記録媒体を作製した。

【0106】実施例9

実施例1において、インク受容層配合Aに替えてインク受容層配合Eを使用した他は、実施例1と同様にして実施例9のインクジェット記録媒体を作製した。

【0107】実施例10

実施例2において、インク受容層配合Aに替えてインク受容層配合Eを使用した他は、実施例2と同様にして実施例10のインクジェット記録媒体を作製した。

【0108】実施例11

実施例1において、インク受容層配合Aに替えてインク受容層配合Fを使用した他は、実施例1と同様にして実施例11のインクジェット記録媒体を作製した。

【0109】実施例12

実施例2において、インク受容層配合Aに替えてインク受容層配合Fを使用した他は、実施例2と同様にして実施例12のインクジェット記録媒体を作製した。

【0110】実施例13

実施例1において、インク受容層配合Aに替えてインク受容層配合Gを使用した他は、実施例1と同様にして実施例13のインクジェット記録媒体を作製した。

【0111】実施例14

実施例2において、インク受容層配合Aに替えてインク受容層配合Gを使用した他は、実施例2と同様にして実施例14のインクジェット記録媒体を作製した。

【0112】実施例15

支持体Bのバライタ塗工層を設けた側に、インク受容層

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【0113】実施例16

支持体Bのバライタ塗工層を設けた側に、インク受容層配合Aの塗工液をカーテンコーターにより乾燥塗工量15g/m²になるように塗工、乾燥し、その上に熱可塑性有機高分子微粒子含有層配合Bの塗工液をカーテンコーターにより乾燥塗工量10g/m²になるように塗工、乾燥した。次いで密度0.962g/cm³の高密度ポリエチレン樹脂を320℃で熔融し、支持体のインク受容層を設けてない面に厚さ30μmになるように押出コーティングし、組面クーリングロールを用いて光沢度5%の裏面樹脂被覆をして耐水層を作成し、実施例16のインクジェット記録媒体を作製した。

【0114】実施例17

実施例15において、インク受容層配合Aに替えてインク受容層配合Bを使用した他は、実施例15と同様にして実施例17のインクジェット記録媒体を作製した。

【0115】実施例18

実施例16において、インク受容層配合Aに替えてインク受容層配合Bを使用した他は、実施例16と同様にして実施例18のインクジェット記録媒体を作製した。

【0116】実施例19

実施例15において、インク受容層配合Aに替えてインク受容層配合Cを使用した他は、実施例15と同様にして実施例19のインクジェット記録媒体を作製した。

【0117】実施例20

実施例16において、インク受容層配合Aに替えてインク受容層配合Cを使用した他は、実施例16と同様にして実施例20のインクジェット記録媒体を作製した。

【0118】実施例21

実施例15において、インク受容層配合Aに替えてインク受容層配合Dを使用した他は、実施例15と同様にして実施例21のインクジェット記録媒体を作製した。

【0119】実施例22

実施例16において、インク受容層配合Aに替えてインク受容層配合Dを使用した他は、実施例16と同様にして実施例22のインクジェット記録媒体を作製した。

【0120】実施例23

実施例15において、インク受容層配合Aに替えてインク受容層配合Eを使用した他は、実施例15と同様にして実施例23のインクジェット記録媒体を作製した。

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ク受容層配合Fを使用した他は、実施例16と同様にして実施例26のインクジェット記録媒体を作製した。

【0124】実施例27

実施例15において、インク受容層配合Aに替えてインク受容層配合Gを使用した他は、実施例15と同様にして実施例27のインクジェット記録媒体を作製した。

【0125】実施例28

実施例16において、インク受容層配合Aに替えてインク受容層配合Gを使用した他は、実施例16と同様にして実施例28のインクジェット記録媒体を作製した。

【0126】比較例1

実施例1において、裏面の耐水層を設けなかった他は実施例1と同様にして、比較例1のインクジェット記録媒体を作製した。

【0127】比較例2

実施例15において、裏面の耐水層を設けなかった他は実施例15と同様にして、比較例2のインクジェット記録媒体を作製した。

【0128】比較例3

実施例1において、裏面の耐水層に替えて、市販の1級カオリン50部、市販のステレン-ブタジエン系ラテックス50部、市販の酸化亜鉛5部を固形分濃度50%で調整して得た塗料組成物をエアナイフコーターを用いて、乾燥塗工量15g/m²となるように塗工乾燥した他は、実施例1と同様にして、比較例3のインクジェット記録媒体を作製した。

【0129】＜インクジェット記録物の作製＞上記により得られたインクジェット記録媒体に、エプソン社製カラーインクジェットプリンタ（PM-770C）を用い、4原色のべた印字及び高精細な写真画像の記録を行い、ついで、120℃に加熱して、最表層を熔融し被膜化した。このようにして作製したインクジェット記録物について、下記の評価方法により評価し、その結果をまとめて表1に示す。

【0130】＜インク吸収性＞高精細な写真画像を描画した部分のインクの溢れや、しみ具合を目視で評価し、優れているものを○、一般的なものを△、使用に耐えないものを×とした。

【0131】＜画像色彩性＞記録画像の画質は、最表層を熔融化した後の、画像が完全にクリアに見えるもの

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【表1】

試料No.	吸 収 性	色 彩 性	耐 水 性	試料No.	吸 収 性	色 彩 性	耐 水 性
実施例 1	◎	○	○	実施例 15	◎	○	○
実施例 2	○	◎	○	実施例 16	○	◎	○
実施例 3	◎	○	○	実施例 17	◎	○	○
実施例 4	○	◎	○	実施例 18	○	◎	○
実施例 5	◎	○	○	実施例 19	◎	○	○
実施例 6	○	◎	○	実施例 20	○	◎	○
実施例 7	◎	○	○	実施例 21	◎	○	○
実施例 8	○	◎	○	実施例 22	○	◎	○
実施例 9	◎	○	○	実施例 23	◎	○	○
実施例 10	○	◎	○	実施例 24	○	◎	○
実施例 11	◎	○	○	実施例 25	◎	○	○
実施例 12	○	◎	○	実施例 26	○	◎	○
実施例 13	◎	○	○	実施例 27	◎	○	○
実施例 14	○	◎	○	実施例 28	○	◎	○
比較例 1	◎	○	×				
比較例 2	○	◎	×				
比較例 3	○	○	△				

【0134】表1の結果から、本発明の実施例の如くインク受容層下層にコロイダルシリカ、気相法シリカ、アルミナ水和物、γ型酸化アルミニウム微粒子を含有し、上層に熱可塑性有機高分子微粒子層を設け、更にその反対側の面に熱可塑性樹脂の溶融押出し法による耐水層を設けたインクジェット記録媒体に画像記録後、熱をかけて熱可塑性有機高分子微粒子層を熱で皮膜化した記録物は、色彩性、吸収性、耐水性共に全て良好であるが、耐水層を設けてない比較例1、2は耐水性で劣り、更に比

較例3は溶融押出し法によらない樹脂層を設けたが、やはり耐水性が悪く実用的でない。

【0135】

【発明の効果】以上から、本発明によれば、印字後加熱することで、表面が溶融樹脂で被覆され、しかも裏側からの水の浸透による影響も排除されている為、極めて耐水性の良いインクジェット記録物が得られ、更に色彩性、インク吸収性にも優れたインクジェット記録媒体が得られる。

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(54) INK JET RECORDING MEDIUM, ITS MANUFACTURE, AND PREPARATION OF RECORDED ARTICLE USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an ink jet recorded article wherein an ink jet image being excellent in ink absorbing property and image coloring property can be obtained in an ink jet recording method, and of which the water-resistance is favorable even when being used outdoor or the like.

SOLUTION: This recording medium is constituted in such a manner that on a supporting body, an ink receiving layer and a layer mainly containing a thermoplastic organic polymeric particle on the top of the ink receiving layer, are provided, and on the opposite surface of the ink receiving layer through the supporting body, at least one layer of a water-resistant layer is provided. In this case, the ink receiving layer is a porous layer which mainly contains an inorganic particle. Also, the water-resistant layer is provided by a melt- extrusion method of a thermoplastic resin for this ink jet recording medium, and the thermoplastic organic polymeric particle layer is a layer to which a thermoplastic organic polymeric particle is fused by melting or fusing it by heating or the like.

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CLAIMS

[Claim(s)]

[Claim 1] The ink jet record medium which is the porous layer in which this ink absorbing layer mainly contains a non-subtlety particle in the ink jet record medium with which it comes to prepare at least one or more-layer waterproof layer in the field which prepares the layer which mainly contains a thermoplastic organic macromolecule particle an ink absorbing layer and on it, and has not prepared the ink absorbing layer of a base material on a base material, and is characterized by preparing this waterproof layer by the melting extrusion method of thermoplastics.

[Claim 2] The ink jet record medium according to claim 1 whose non-subtlety particle of this ink absorbing layer is at least one sort chosen mainly from the group of colloidal silica, hydrated alumina, gamma mold aluminum oxide, and a gaseous-phase method silica.

[Claim 3] The ink jet record medium according to claim 1 whose non-subtlety particle of this ink absorbing layer is hydrated alumina which has un-spherical colloidal silica or pseudo-boehmite structure.

[Claim 4] The ink jet record medium of claim 1-3 this whose base material is with an or more [120g //m] 2 basis weight non-coated paper or coated paper given in any 1 term.

[Claim 5] An ink jet record form given in any 1 term of claims 1-4 this whose thermoplastics is polyolefin resin.

[Claim 6] The ink jet record form according to claim 5 this whose polyolefin resin is either polyethylene resin or polypropylene resin.

[Claim 7] The layer which mainly contains a thermoplastic organic macromolecule particle an ink absorbing layer and on it is prepared on a base material. In the manufacture approach of an ink jet record medium of coming to prepare at least one or more-layer waterproof layer in the reverse side of this ink absorbing layer through a base material The manufacture approach of the ink jet record medium characterized by preparing a waterproof layer in the reverse side through the base material by the melting extrusion method of thermoplastics after preparing an ink absorbing layer and the layer which contains a thermoplastic organic macromolecule particle on it.

[Claim 8] The creation approach of the record object characterized by considering as the layer which dissolved or dissolved the layer containing this thermoplastic organic macromolecule particle to the ink jet record medium according to claim 1 to 7 after ink jet record, and this thermoplastic organic macromolecule particle welded to it.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is the ink jet record medium which prepared the waterproof layer in the background which prepared in more detail the layer which contains a thermoplastic organic macromolecule particle on a surface about the ink jet record medium, and minded the base material, and relates to the ink jet record medium with which the outstanding record object of color nature, ink absorptivity, and a water resisting property is obtained by coat-izing the layer containing this thermoplastic organic macromolecule particle after ink jet record.

[0002]

[Description of the Prior Art] Although an ink jet recording method makes the minute drop of ink fly by various working principles, and is made to adhere to record media, such as paper, and an image, an alphabetic character, etc. are recorded, the development-fixation with the large versatility of ease [a high speed, the low noise, and multiple-color-izing] and a record pattern has the descriptions, such as needlessness, and has spread quickly in various applications including the kanji as recording devices, such as various graphic forms and a color picture. Moreover, since the image formed by the multicolor ink jet method is cheap rather than it is possible to acquire equal record as compared with the print by process printing by the platemaking method or the color photography method and creation number of copies is further based on a photograph technique in the application which there are and ends, it is being widely applied even to the full color image recording field. [few]

[0003] Efforts have been made from equipment or the field of an ink presentation in order to use the paper of fine quality and coated paper which are used for usual printing and a usual note as a record medium used by the ink jet recording method. However, a more advanced property came to be required also from the record medium with improvement in engine performance of an ink jet recording device, such as improvement in the speed and highly-minute-izing, or full-color-izing of equipment, or amplification of an application. Namely, as the record medium concerned, the concentration of a printing dot is high and a color tone is brightly skillful, When absorption of ink is early and a printing dot laps, and it does not spread or don't carry out, [that ink flows out] The diffusion to the longitudinal direction of a printing dot is uniform, and it is not large beyond the need, and to excel in that there is no change of image quality, for example, lightfastness, a water resisting property, and ozone resistance etc. is demanded in that the circumference is smooth and does not fade, and the passage of time and an environment.

[0004] Some proposals have been performed from the former to such a demand. Paying attention to the distribution condition of the color component in the approach of preparing an ink absorbing layer on a base material to the improvement in ink absorptivity or diffusion prevention of a printing dot, and the ink in an ink absorbing layer (JP,52-9074,A, 58-72495 official report, etc.) influencing color nature and sharp nature, the approach (JP,55-144172,A) using specific ** which adsorbs a color component etc. is shown. Moreover, in order to raise lightfastness, a water resisting property, and ozone resistance, using a polyvinyl amine copolymerization object for the coating layer in making basic oligomer contain (JP,60-11389,A) and a base material or on a base material (JP,64-8085,A) etc. is indicated.

[0005] It follows on diversification of an application. Furthermore, it is used for a poster

or a POP art, or A binder layer is prepared in a rear face. The label for a price display, the label for a goods display (bar code), It pastes up to the adherend of label applications, such as a label for a quality display, a label for a measuring display, and an advertising spot label (sticker), and the large range well. Since the attachment activity is easy, since it becomes possible to also make the function which stuck with the sheet which is alike on the other hand and has a sensible-heat property, magnetic properties, and offset-printing fitness through an adhesive layer, and was compounded add, the application to a ticket, a commuter pass, various cards, etc. is also spreading.

[0006] However, while the demand to these properties became altitude gradually and it became severe, in the application used for a large-sized poster etc., these were used outdoors, and it is exposed to a rainstorm or was also exposed to direct sunlight more often. Therefore, an ink jet record medium may be required to also hold the capacity that these environments can be opposed.

[0007] By the ink jet recording method, the ink which dissolves or distributed the color and the pigment has been used into a water or oily solvent as ink from the former. The water-soluble-dye ink made to dissolve various kinds of water soluble dye in the mixture of water or water, and an organic solvent especially is in use. Water-soluble-dye ink is excellent in the maintenance nature of the ink discharge head of an ink jet recording device, and excellent in the color enhancement after printing, resolution, etc. However, therefore water-soluble **** is and a problem is in the water resisting property of a record image. Moreover, especially since weatherability (fading and disappearance of an image by light, air, and temperature and humidity) is originally inferior, water soluble dye has the fault which an image fades quickly [the case where outdoor display of the record medium is carried out], or disappears.

[0008] It is divided roughly into the regular paper type represented by the so-called paper of fine quality, bond paper, etc. and the coating type which prepared the ink absorbing layer on base material sides, such as papers, such as paper of fine quality, a synthetic paper, and a synthetic-resin film, as a gestalt of an ink jet record medium. A coating type ink jet record medium from the thing of the painted ink absorbing layer for which a property influences a quality of printed character directly variously As opposed to absorptivity about selection of the specific surface area of a pigment, or a configuration, color nature, or color repeatability Examination of the transparency of a pigment, or a refractive index, To image quality, if, examination has been variously made about various examination called combination of underwater ductility, a synthetic fiber, or a glass fiber about the improvement of flapping of a form etc., such as the shape of coated layer structure or surface type, the coating approach, etc.

[0009] Furthermore, after ink jet record, stick a film on a front face, coating of the clear resin layer is carried out, or the layer of a thermoplastic organic giant-molecule particle is beforehand prepared in the ink absorbing layer front face, and the attempt (JP,59-201891,A, JP,62-183383,A, JP,01-182055,A, JP,01-182081,A, JP,02-81663,A, JP,07-237348,A) which is going to acquire a water resisting property and gloss is also made by fusing this thermoplastic organic giant-molecule particle after ink jet record. Although there are various approaches, such as letting between the rolls, application of pressure and heating, of two pass, or it is stuck to a heat drum like the ferrotype dryer used for desiccation of the baryta photographic printing paper as an approach of carrying out eburnation of the layer of a thermoplastic organic giant-molecule particle after printing

by pressure, eburnation is carried out by being stuck to the smooth metal roll generally heated by pressure in many cases. Although it was the proposal of having dissolved or dissolved, and a thermoplastic organic macromolecule particle layer having been formed by this eburnation processing, and acquiring a water resisting property, weatherability, glossiness, or transparency, this thermoplastic organic macromolecule particle will adhere to the front face of a heat drum or a hot calender roll, or consideration is required for osmosis of the water from a flesh side etc., or there is a thing problem, and the further improvement was called for.

[0010]

[Problem(s) to be Solved by the Invention] The ink jet image which was excellent in ink absorptivity and image color nature in the ink jet recording method is obtained, and this invention aims at offering an ink jet record object with a water resisting property sufficient even when it is used outdoors etc.

[0011]

[Means for Solving the Problem] In order that this invention persons may attain said technical problem, as a result of inquiring wholeheartedly, the layer which mainly contains a thermoplastic organic macromolecule particle an ink absorbing layer and on it is prepared on a base material. In the ink jet record medium with which it comes to prepare at least one or more-layer waterproof layer in the field in which the ink absorbing layer of a base material is not established It came to complete header this invention for the ink jet record object which is the porous layer in which this ink absorbing layer mainly contains a non-subtlety particle, and can attain said object by preparing this waterproof layer by the melting extrusion method of thermoplastics being obtained.

[0012] This non-subtlety particle is more desirable in it being at least one sort mainly chosen from the group of colloidal silica, the amorphous silica particle compounded by the gaseous-phase method, hydrated alumina, and gamma mold aluminum-oxide particle.

[0013] This base material is more desirable in their being two or more basis weight 120 g/m non-coated paper or coated paper.

[0014] The thermoplastics of this waterproof layer is desirable in it being polyolefin resin, and more desirable in polyolefin resin being polyethylene resin or polypropylene resin further.

[0015] Moreover, the layer which mainly contains a thermoplastic organic macromolecule particle an ink absorbing layer and on it is prepared on a base material. In the manufacture approach of an ink jet record medium of coming to prepare at least one or more-layer waterproof layer in the reverse side of this ink absorbing layer through a base material After preparing an ink absorbing layer and the layer which contains a thermoplastic organic macromolecule particle on it, it is the manufacture approach of the ink jet record medium characterized by preparing a waterproof layer in the reverse side through the base material by the melting extrusion method of thermoplastics.

[0016] Furthermore, it is the creation approach of the record object characterized by considering as the layer in which the layer which contains this thermoplastic organic macromolecule particle after ink jet record was dissolved or dissolved to the ink jet record medium of above-mentioned this invention, and this thermoplastic organic macromolecule particle welded it to it with heating etc.

[0017]

[Embodiment of the Invention] Hereafter, the ink jet record medium of this invention is

explained to a detail. The ink jet record medium used by this invention is the configuration of having prepared thermoplastics in the opposite hand which it has the layer which contains a thermoplastic organic macromolecule particle on a surface, and the porous ink absorbing layer which mainly contains a non-subtlety particle is between a base material and the layer containing a thermoplastic organic macromolecule particle, and minded the base material further by the melting extrusion method.

[0018] Although the paper and coated paper which especially a limit does not have and are generally used as a base material of the above-mentioned record medium can be used, preferably, it is smooth and is coated paper which is used for the base material for photographs and which prepared the pigment coating layer paper with a high consistency, and on it. as the pulp which constitutes paper -- natural pulp, playback pulp, a synthetic pulp, etc. -- one sort -- or two or more sorts are mixed and it is used. As natural pulp, each ** chemical pulp, such as the pulp usually used for paper making, i.e., needle-leaf tree kraft pulp, broad-leaved tree kraft pulp, a needle-leaf tree sulfite pulp, and a broad-leaved tree sulfite pulp, etc. is usable. Moreover, a whiteness degree may be a high mechanical pulp. Furthermore, the non-wood pulp manufactured from bast fiber, such as grass fiber, such as straw, S PARUTO, a bagasse, and a kenaf, hemp, a paper mulberry, ganpi, and a paper birch, cotton, etc. is sufficient. In these, especially ** chemical pulps, such as needle-leaf tree kraft pulp usually industrially used abundantly most, broad-leaved tree kraft pulp, a needle-leaf tree sulfite pulp, and a broad-leaved tree sulfite pulp, are desirable.

[0019] In order that pulp may raise many properties of papers of paper-making fitness and reinforcement, smooth nature, and formation, such as homogeneity, etc., usually beating is carried out by beaters, such as a double disc refiner. Extent of beating is a Canadian. Standard According to the object, it can usually choose in 250ml - 450ml by freeness.

[0020] Although paper making of the pulp slurry by which beating was carried out is carried out by paper machines, such as a Fortlinear paper machine, a twin-wired paper machine, or a cylinder machine, many additives, such as the distributed assistant of the pulp slurry usually used on the occasion of paper making in this invention, a desiccation paper reinforcing agent, a humid paper reinforcing agent, a loading material, a sizing compound, and a fixing agent, can be altogether added if needed in this case.

Furthermore, it is required and that can add a pH regulator, a color, a colored pigment, a fluorescent brightener, etc.

[0021] As a distributed assistant, for example, polyethylene oxide, polyacrylamide, grated yam -- ***** etc. -- as a paper reinforcing agent -- for example, anionic paper reinforcing agents, such as vegetable gum, starch, and carboxy denaturation polyvinyl alcohol, -- Cationic paper reinforcing agents, such as cation-ized starch, cationic polyacrylamide, and a polyamide polyamine epichlorohydrin resin As a loading material, for example, clay, a kaolin, talc, a calcium carbonate, a barium sulfate, Titanium oxide, an aluminum hydroxide, a magnesium hydroxide, etc. as a sizing compound For example, a higher-fatty-acid salt, Rosin derivatives, such as rosin and mallein-ized rosin, a dialkyl ketene dimer, The alkenyl or alkyl succinate, an epoxidation fatty-acid amide, polysaccharide ester, etc. As a fixing agent, cationic polymers, such as polyvalent metallic salt, such as an aluminum sulfate and an aluminum chloride, cation-ized starch, and a polyamide polyamine epichlorohydrin resin, etc. are used, and a hydrochloric acid,

caustic alkali of sodium, sodium carbonate, etc. are used as a pH regulator.

[0022] Moreover, the paper base material used for this invention is the liquid containing various kinds of additives including a water soluble polymer additive, and can also carry out [Tab size or] size press.

[0023] As the above-mentioned water soluble polymer additive, for example Starch, cation-ized starch, oxidized starch, Starch derivatives, such as etherification starch and phosphoric ester-ized starch, polyvinyl alcohol, Polyvinyl alcohol derivatives, such as carboxy denaturation polyvinyl alcohol, Carboxymethylcellulose, a hydroxymethyl cellulose, a hydroxyethyl cellulose, Cellulosics, such as cellulose sulfate, gelatin, casein, Water-soluble naturally-occurring polymers, such as soybean protein, sodium polyacrylate, styrene-maleic-anhydride copolymer sodium salt, Water soluble polymers, such as maleic-anhydride resin, such as polystyrene specific sulfonate, Aquosity macromolecule adhesives, such as thermosetting synthetic resin, such as melamine resin and a urea-resin, etc. are used. Further in addition to this, as a sizing compound, a petroleum resin emulsion, the ammonium salt of styrene-maleic-anhydride copolymer alkyl ester, DISUPASHON, such as an alkyl ketene dimer emulsification object, a styrene-butadiene copolymer, an ethylene-vinylacetate copolymer, polyethylene, and a polyvinylidene chloride, is mentioned. As other additives, the sodium chloride which is an inorganic electrolyte, a calcium chloride, Glauber's salt, etc. are possible also for clay, a kaolin, talc, a barium sulfate, titanium oxide, etc. being used as a pigment, and a hydrochloric acid, caustic alkali of sodium, sodium carbonate, etc. being used as a pH regulator, in addition a glycerol, a polyethylene glycol, etc. using it combining additives, such as a color, a fluorescent brightener, an antioxidant, and an ultraviolet ray absorbent, as hygroscopic matter, as an antistatic agent.

[0024] Moreover, the good thing of surface smooth nature of the paper base material used for this invention carried out [compress / during paper milling or after paper milling / a pressure / in a calender etc. / impress and] is desirable, and especially the thing for 200 seconds or more has Beck's desirable smoothness measured by JIS-P -8119.

[0025] Moreover, coated paper, such as the art paper and coat paper which prepared the coating layer containing white pigments on the above-mentioned paper as a coated paper base material which can be used by this invention, a cast-coated paper, and a baryta paper, is mentioned.

[0026] As white pigments used for the coating layer of a coated paper base material, various well-known pigments can be used conventionally. For example, a silica, an alumina or hydrated alumina, aluminum silicate, A magnesium silicate, a magnesium carbonate, precipitated calcium carbonate, whiting, A kaolin, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, A zinc oxide, zinc sulfide, zinc carbonate, a satin white, the diatom earth, a calcium silicate, An aluminum hydroxide, a lithopone, a zeolite, hydrated halloysite, a magnesium hydroxide, Organic pigments, such as which inorganic pigment and also a styrene system plastics pigment, an acrylic plastics pigment, polyethylene, a microcapsule, a urea-resin, and melamine resin, etc. can be mentioned. Especially, since a barium sulfate, a titanium dioxide, and a zinc oxide can form a uniform coating layer with high opacity and uniform particle diameter, they are desirable.

[0027] Moreover, it is the thing of two or more 120 g/m basis weight that the basis weight of a base material is preferably used by this invention although an about two 30 - 300 g/m thing is used.

[0028] When the diameter of a primary particle is a non-subtlety particle 100nm or less, and condenses, or they connect the non-subtlety particle in the ink jet record medium of this invention and form the aggregated particle, the second [an average of] particle diameter says a thing 20 micrometers or less. For example, an amorphous silica particle, hydrated alumina, etc. are mentioned. As an amorphous silica, they are the so-called white carbon, silica gel, an impalpable powder silica, etc. Moreover, as hydrated alumina, they are amorphism alumina sol, pseudo-boehmite, etc. If it says, furthermore, JP,1-97678,A, a 2-275510 official report, A 3-281383 official report, a 3-285814 official report, a 3-285815 official report, The pseudo-boehmite sol proposed by the 4-92183 official report, the 4-267180 official report, the 4-275917 official report, etc., JP,60-219083,A, a 61-19389 official report, a 61-188183 official report, Colloidal silica which is indicated by a 63-178074 official report, JP,5-51470,A, etc., The silica / alumina hybrid sol which is indicated by JP,4-19037,B and JP,62-286787,A, As [indicate / by JP,10-119423,A and JP,10-217601,A] A silica sol which distributed the ultrafine particle silica with the high-speed homogenizer, In addition, smectite clay (JP,7-81210,A), such as Hector Ito and a montmorillonite, a zirconia sol, a chromia sol, a yttria sol, a ceria sol, a ferrous-oxide sol, a zircon sol, an antimony oxide sol, etc. can be mentioned as a typical thing.

[0029] A commercial non-subtlety particle can also be suitably used for the ink jet record medium of this invention. Although the example is given to below, this invention is not limited to this. For example, as hydrated alumina, it is KATAROIDO AS-1, KATAROIDO AS-2, and KATAROIDO AS-3 (above). The alumina sol 100 made from the catalyst chemical industry, alumina sol 200, alumina sol 520 (above) The Nissan Chemical Industries make, M-200 (above, Mizusawa Industrial Chemicals make), the aluminum sol 10, the aluminum sol 20, the aluminum sol 132, aluminum sol 132S, As the aluminum sol SH5, the aluminum sol CSA 55, the aluminum sol SV 102, the aluminum sol SB 52 (above, Kawaken Fine Chemicals make), and colloidal silica The Snow tex 20, the Snow tex 30, the Snow tex 40, the Snow tex S The Snow tex O, the Snow tex C, the Snow tex N, Snow tex 20L, The Snow tex UP, the Snow tex OL, the Snow tex AK, Snow tex PST-1, the Snow tex K The Snow tex XS, the Snow tex SS, the Snow tex XL, the Snow tex YL, The Snow tex ZL, Snow tex PST-1, Snow tex PST-3, Snow tex PST-5, MA-ST, IPA-ST, NBA-ST, IBA-ST, EG-ST, XBA-ST, ETC-ST, DMAC-ST (above, Nissan Chemical Industries make), KATAROIDO S-20L, KATAROIDO S-20H, KATAROIDO S-30L, KATAROIDO S-30H, KATAROIDO SI-30, KATAROIDO SI-40, KATAROIDO SI-50, KATAROIDO SI-350, KATAROIDO SI-45P, KATAROIDO SI-80P, KATAROIDO SN, KATAROIDO SA, KATAROIDO SB USB-1, USB-2, USB-3, OSCAL1132, OSCAL1232, OSCAL1332, OSCAL1432, OSCAL1532, OSCAL1622, OSCAL1722 (above) a catalyst -- formation -- as the product made from industry, and a silica / alumina hybrid sol As Snow tex UP-AK1, Snow tex UP-AK2, Snow tex UP-AK3 (above, Nissan Chemical Industries make), and an antimony oxide sol As A-1530, A-1550, A-2550 (above, Nissan Chemical Industries make), and lithium silicate, lithium silicate 35, lithium silicate 45, lithium silicate 75 (above, Nissan Chemical Industries make), etc. can be mentioned.

[0030] Colloidal silica, a gaseous-phase method silica ultrafine particle, hydrated alumina, or gamma mold aluminum-oxide particle can be suitably used also especially in these non-subtlety particles.

[0031] Generally the configuration of the colloidal silica which is one of the non-subtlety particles is carrying out the near configuration spherically or spherically. The colloidal silica concerning this invention has the desirable thing of the long and slender configuration which the small silica particle connected in the shape of a chain, or the shape of a non-ball which has the three-dimensional network. The particle of a long and slender configuration does not have expanding in the direction of three dimensions, but means what was elongated in the same flat surface. An almost straight thing, a straight thing, the thing that has branching, the thing which has a ring are contained in the particle of a long and slender configuration. On the other hand, the particle which has a three-dimensional network points out what has the network structure round which the particle of these long and slender configurations twined literally in three dimensions.

[0032] The silica particle of the shape of a non-[these] ball preferably used for this invention is obtained by various approaches, and no matter it may be obtained by what approach in this invention, if the silica particle has the shape of a non-ball, it can be preferably used for this invention. as the formation approach of a non-ball-like silica particle -- for example, common water glass to alkalinity -- removing -- activated silica -- carrying out -- un--- being spherical (the shape of a chain) -- it is obtained by adding the cation more than divalent and growing up a particle so that it may connect.

[0033] Activated silica is a colloidal particle with which the polymer of silicic acid and silicic acid with a particle diameter of less than 3nm coexists here, and it is easily obtained by the well-known approach. The desirable colloid water solution of activated silica is obtained by carrying out cation-exchange processing of the diluent of the water glass whose water-soluble silicate, for example, a $\text{SiO}_2/\text{M}_2\text{O}$ (however, M shows alkali-metal atom) mole ratio, is one to about 4.5, it usually contains one to 6% of the weight preferably 6 or less % of the weight by SiO_2 conversion, and what is 2-5 preferably is usually used five or less pH. This pH can be easily prepared also also making some cations in it remain, or by adding a little alkali-metal oxide, a water-soluble organic base, etc. to the colloid water solution of the activated silica obtained after removing all or some of cations in it, in case cation-exchange processing of the above-mentioned water glass diluent is carried out. The colloid liquid of this activated silica is unstable, and what solves and does not contain an impurity if possible although this gelation is promoted, since it has the property which is easy to gel is desirable, and its thing immediately after preparation is desirable. The still more desirable colloid water solution of activated silica is obtained by passing hydrogen mold cation exchange resin in the dilution water solution of the sodium water glass which is the commercial industrial product whose $\text{SiO}_2 / \text{Na}_2\text{O}$ mole ratio are two to about four.

[0034] the colloid water solution of this activated silica -- un--- being spherical (the shape of a chain) -- the cation more than divalent is added and a particle is grown up so that it may connect. As a cation more than divalent, calcium ion and magnesium ion are desirable, it is the gestalt of a calcium salt, magnesium salt, or those mixture, and adding as a water solution is desirable. Especially in the case of 1500-25000 ppm and a long and slender particle, in the weight ratio $[(\text{CaO}+\text{MgO}) / \text{SiO}_2]$ converted as each oxide to the above-mentioned activated silica as a total amount of this calcium salt, magnesium salt, or those mixture, the amount used as 1500-8500 ppm is desirable.

[0035] Moreover, it is good to perform addition of these salts to the bottom of churning of the colloid liquid of activated silica, and although there is especially no limit in the

mixed temperature and time amount in that case, about 5 - 30 minutes is desirable at 2-50 degrees C. As an example of the calcium salt added and magnesium salt, an inorganic-acid salt and organic-acid salts, such as the chloride of calcium or magnesium, a nitrate, a sulfate, sulfamate, formate, and acetate, are mentioned. These calcium salt and magnesium salt may be mixed and used. Moreover, as concentration at the time of addition of these salts, there is especially no limit and it is good at about 2 - 20 % of the weight.

[0036] If polyvalent metal components other than calcium and magnesium are contained in the colloid liquid of the above-mentioned activated silica with these calcium salt, magnesium salt, etc., a silica sol can be manufactured still more preferably. As an example of polyvalent metal other than this calcium and magnesium, divalent [, such as Sr, Ba, Zn, Sn, Pb Cu, Fe, nickel, Co, Mn, aluminum, Cr, Y, and Ti,] and a trivalent or tetravalent metal are mentioned. As an amount of these polyvalent metal component, when the amount of a calcium salt and magnesium salt is converted into the amount of CaO and MgO, respectively, about 10 - 80 % of the weight is desirable as a polyvalent metal oxide to these [CaO and MgO].

[0037] When the amount of above-mentioned polyvalent metal remains in the colloid liquid of the activated silica obtained by carrying out cation-exchange processing of the diluted solution of the above-mentioned water glass, a part for this polyvalent metal is included as a part of 10 - 80 above-mentioned % of the weight. As for a part for the polyvalent metal of the remainder, it is desirable to add together with a calcium salt, magnesium salt, etc. which are added as a water solution of the above-mentioned polyvalent metal. As a desirable example of this polyvalent metal, inorganic-acid salts and organic-acid salts, such as a chloride, a nitrate, a sulfate, sulfamate, formate, and acetate, are mentioned. Moreover, salts [, such as a sodium aluminate for example, sodium stannate etc.,], such as a zincate, stannate, an aluminate, and a plumbate, can also be used. As for the above-mentioned calcium salt added, magnesium salt, polyvalent metallic salt, etc., it is desirable to mix to the colloid liquid and the homogeneity of activated silica, and they are usually added as a water solution.

[0038] An alkali-metal hydroxide, water-soluble organic bases, or those water-soluble silicate is added to the aqueous liquid obtained according to the above-mentioned process. It is desirable to perform this addition to the bottom of early and churning if possible after termination of the above-mentioned process. Moreover, although there is especially no limit in the temperature and time amount of these mixing, about 5 - 30 minutes is desirable at 2-50 degrees C. As for the alkali-metal hydroxide added, water-soluble organic bases, or those water-soluble silicate, it is desirable that homogeneity is mixed with the aqueous liquid obtained according to the above-mentioned process, and it is added as direct or a water solution.

[0039] As an alkali-metal hydroxide, hydroxides, such as sodium, a potassium, and a lithium, are mentioned, for example. As an organic base, the organic compound of amines, such as the 4th class ammonium hydroxides, such as a tetra-ethanol ammonium hydroxide, a monomethyl triethanol ammonium hydroxide, and a tetramethylammonium hydroxide, monoethanolamine, diethanolamine, triethanolamine, N,N-dimethylethanolamine, N-(beta-aminoethyl) ethanolamine, N-methylethanol amine, mono-propanolamine, and a morpholine, and other basic nitrogen atom content etc. is mentioned, for example. Moreover, as those water-soluble silicate, the silicate of a

specific silicate, a potassium silicate, and the above-mentioned 4th class ammonium, the silicate of the above-mentioned amine, etc. are illustrated.

[0040] Furthermore, alkali metal or the aluminate of an organic base, formate, a zincate, a plumbate, etc. can be used. These alkali-metal hydroxide, an organic base, silicate, metal acid chloride, etc. may be mixed and used. If the alkali-metal atom of the above-mentioned alkali-metal hydroxide or the molecule of an organic base is expressed with M, the amount of the alkali-metal hydroxide added, organic bases, or those water-soluble silicate sets the sum total for a part for the silica originating in activated silica, and the silica of silicate to SiO_2 , and 20-200, and its amount that serves as a mole ratio of 60-100 preferably are $[\text{SiO}_2/\text{M}_2\text{O}]$ good. By this addition, liquid comes to show about seven to ten pH.

[0041] The silica sol which has the configuration of the shape of a non-ball of 1 - 6 % of the weight of SiO_2 concentration is obtained by heating preferably the mixture obtained according to the above process at 90-150 degrees C by 60-300 degrees C for 2 to 12 hours for 30 minutes to 40 hours. A high concentration sol is obtained by condensing this sol by request. In addition, the diameter of an aggregated particle measured by dynamic light scattering is the range which is 40-300nm, and according to electron microscope observation, the silica particle of the shape of a non-ball acquired by the above-mentioned approach has the inside of 1 flat surface, or the configuration where it grew up in three dimensions, by the 5-40nm size.

[0042] In coating liquid for the silica particle of the shape of a non-ball concerning this invention to form the ink absorbing layer in the ink jet record medium of this invention at least Preparation of the coating liquid for ink absorbing layer formation is preceded that what is necessary is just to exist in the non-ball-like configuration. The silica particles of the shape of a non-ball concerning this invention including the above-mentioned approach may be prepared, and the coating liquid for ink absorbing layer formation may be prepared using this, and you may prepare coating liquid, preparing the silica particles of the shape of a non-ball concerning this invention including the above-mentioned approach in coating liquid at the time of the coating liquid preparation for ink absorbing layer formation. A commercial thing can also be used if the silica particle of the shape of a non-ball concerning this invention is beforehand prepared before coating liquid preparation. As an example of the silica particle of the shape of a commercial non-ball, the Nissan Chemical Industries Snow tex UP, the Snow tex OUP, etc. are mentioned.

[0043] Silica particles other than colloidal silica have amorphous silicas, such as the so-called white carbon, silica gel, and an impalpable powder silica. As the manufacture approach of an amorphous silica particle, there are a liquid phase process, a grinding solid phase technique, a crystallization solid phase technique, and a gaseous-phase method. A liquid phase process is the particle manufacture approach of depositing the silicic acid compound which exists in the so-called liquid in a solid state according to a chemical change or a physical change. A grinding solid phase technique is the approach of grinding a silica solid-state mechanically, and a crystallization solid phase technique is the particle manufacture approach of having used melting, solid phase transition, etc. A gaseous-phase method is the particle manufacture approach by the pyrolysis of the steam of volatile metallic compounds, heating of a raw material, cooling of the gaseous-phase kind evaporated and generated, and condensation.

[0044] The silica particle used by this invention has the desirable amorphous silica

particle compounded by the gaseous-phase method among the above. The ultrafine particle-like silica whose first [an average of] particle diameter is 3nm - 100nm especially is desirable. Especially the desirable diameter of a primary particle is a 4nm - 50nm thing. Moreover, as an aggregated particle which these connected, it is good to make [10nm - 200nm] it more preferably 15nm - 100nm. Aerosil (Degussa AG) corresponds as a product marketed as an amorphous silica particle compounded by this gaseous-phase method.

[0045] A silica particle with the above-mentioned diameter of a primary particle is added in water, a high-speed homogenizer etc. distributes, and the second [an average of] particle diameter distributes preferably 200nm or less of gaseous-phase method silica particle sols used by this invention to 100nm or less.

[0046] The following general formula can express the hydrated alumina used for this invention.

$\text{aluminum}_2\text{O}_3$ and $n\text{H}_2\text{O}$ hydrated alumina are classified into JIPUSAITO, the Bahia light, NORUSUTORANDAITO, boehmite, boehmite gel (pseudo-boehmite), diaspoire, an amorphism amorphous substance, etc. according to the difference in a presentation or a crystalline form. Especially, n exceeds 1, among the above-mentioned formula, when the value of n is 1, the hydrated alumina of boehmite structure is expressed, when it is less than three, the hydrated alumina of pseudo-boehmite structure is expressed, and n expresses the hydrated alumina of amorphous structure or more with three. At least, n exceeds 1 and especially hydrated alumina desirable to this invention is hydrated alumina of less than three pseudo-boehmite structure.

[0047] In order for hydrated alumina to have sufficient ink rate of absorption, it is desirable that the average pore radii of hydrated alumina are 1 thru/or 10nm, and it is desirable especially that they are 3 thru/or 7nm. If a pore radius is too small, absorption of ink will become difficult, if a pore radius is too large, fixation of the color in ink will worsen and a blot of an image will occur.

[0048] In order for hydrated alumina to have sufficient ink absorption capacity, it is desirable that the pore volume of hydrated alumina is the range of 0.3 thru/or 0.8 ml/g, and it is desirable especially that it is the range of 0.4 thru/or 0.6 ml/g. When the pore volume of an ink absorbing layer is large, a crack and powder omission occur in an ink absorbing layer, and absorption of ink becomes slow when pore volume is small. Furthermore, as for especially the solvent absorbed amount of the ink absorbing layer per unit area, it is desirable that they are two or more 10 ml/m two or more 5 ml/m. When the solvent absorbed amount per unit area is small, and process printing is carried out, ink may especially overflow.

[0049] For hydrated alumina fully absorbing the color in ink, and being established, it is desirable that it is the range whose BET specific surface areas are 70 thru/or 300m²/g. If a BET specific surface area is too small, pore volume distribution inclines toward the larger one, the fixation effectiveness of the color in ink worsens, and a blot of an image occurs. On the contrary, if a BET specific surface area is too large, distribution of hydrated alumina will become difficult.

[0050] Any of plate-like, fibrous, a needle, a globular shape, and cylindrical ** are sufficient as the configuration of the hydrated alumina used for this invention, and a desirable configuration is plate-like from a viewpoint of ink absorptivity. Plate-like hydrated alumina is the average aspect ratios 3-8, and average aspect ratios are 3-6

preferably. An aspect ratio is expressed with the ratio of a "diameter" to "thickness" of a particle. A diameter of circle equal to the projected area of the particle when observing hydrated alumina with an electron microscope is expressed as the diameter of a particle here. When an aspect ratio is smaller than the above-mentioned range, the pore volume distribution of an ink absorbing layer becomes narrow, and ink absorptivity falls. On the other hand, when an aspect ratio exceeds the above-mentioned range, it becomes difficult to arrange a particle and to manufacture hydrated alumina.

[0051] The hydrated alumina used for this invention can be manufactured by well-known approaches, such as neutralization by hydrolysis of aluminum alkoxides, such as aluminum isopropoxide, and the alkali of an aluminum salt, and hydrolysis of an aluminate. Moreover, physical properties, such as particle diameter of hydrated alumina, pore size, pore volume, and specific surface area, are controllable by the conditions of deposit temperature, maturing temperature, maturing time, pH of liquid, the concentration of liquid, a coexistence compound, etc.

[0052] As an approach of obtaining hydrated alumina from an alkoxide, it is indicated as an approach of hydrolyzing an aluminum alkoxide on JP,57-88074,A, a 62-56321 official report, JP,4-275917,A, a 6-64918 official report, a 7-10535 official report, a 7-267633 official report, U.S. Pat. No. 2,656,321 descriptions, etc. Isopropoxide, 2-butoxide, etc. are mentioned as these aluminum alkoxides.

[0053] Moreover, the approach of using the mineral salt of aluminum or its hydrate for JP,54-116398,A, a 55-23034 official report, a 55-27824 official report, and a 56-120508 official report as a raw material is indicated. As a raw material, mineral salt, such as an aluminum chloride, an aluminium nitrate, an aluminum sulfate, a polyaluminum chloride, an ammonium alum, a sodium aluminate, potassium aluminate, and an aluminum hydroxide, and the hydrate of those can be mentioned, for example.

[0054] Furthermore, as an option, **** and pH which are indicated by JP,56-120508,A are fluctuated by turns to an acidity thru/or basicity side, the approach of growing up the crystal of hydrated alumina, **** indicated by JP,4-33728,B, the hydrated alumina obtained from the mineral salt of aluminum, and the alumina obtained with a Bayer process are mixed, and there is also a method of rehydrating an alumina.

[0055] If gamma mold aluminum-oxide particle is gamma mold crystal of an aluminum oxide and it classifies crystallographically in this invention, it can divide into gamma group and delta group further. The particle which has delta group's crystalline form is more desirable.

[0056] Although the alumina of gamma mold crystal particle can make mean particle diameter of a primary particle small to about 10nm, generally, a primary particle forms secondary condensation gestalten (it is hereafter described as a secondary particle), and particle diameter becomes large even at thousands to tens of thousands of nm. If gamma mold alumina crystal particle of such large particle diameter is used, although the printing nature of an ink absorbing layer and absorptivity are good, it becomes easy to generate a chip and a paint film defect in transparency. As for the mean particle diameter of a primary particle, it is desirable that it is less than 80nm. If the secondary particle which consists of a primary particle 80nm or more is used, it will very become easy to generate the increase of brittleness, and a paint film defect.

[0057] In order to obtain gamma mold alumina crystal particle sol, mean particle diameter usually grinds 200nm or less of gamma mold alumina crystals used as a

thousands to tens of thousands of nm secondary particle with grinding means, such as a bead mill, and an ultrasonic homogenizer, a high voltage type homogenizer, until it becomes an ultrafine particle 100nm or less preferably. Although ink absorptivity will increase if mean particle diameter exceeds 200nm, a coat is weak and transparency falls. The approach using an ultrasonic homogenizer and a high voltage type homogenizer as a grinding means is desirable, and by other grinding approaches, such as a bead mill, since gamma mold alumina crystal is a hard crystal, it is easy to mix a foreign matter from a grinding container, and becomes lowering of transparency, and the cause of generating of a defect. gamma mold alumina crystal particle is excellent in ink absorptivity, is good, and can obtain the ink jet record medium which was excellent in transparency ultrafine-particle-izing even if it made the ink absorbing layer contain by the high ratio. [of qualities of printed character, such as drying and ink fixable,]

[0058] gamma mold alumina crystal particle can come to hand as a commercial item as aluminum oxide C (product made from Japanese Aerosil) belonging to delta group, AKP-G015 (Sumitomo Chemical Co., Ltd. make) belonging to gamma group, etc.

[0059] As a binder of a non-subtlety particle used for this invention, the high molecular compound of water solubility or nonaqueous solubility may be added. The high molecular compounds used for this invention are ink and a compound which has compatibility as a constituent of an ink absorbing layer. For example, as a water soluble polymer compound, they are polyvinyl alcohol, acrylic resin, a styrene-acrylic copolymer, a maleic-anhydride polymer, a styrene maleic anhydride copolymer, an ethylene-vinylacetate copolymer, starch, a polyvinyl butyral, gelatin, casein, an ionomer, gum arabic, a carboxymethyl cellulose, an alginic acid, sodium alginate, a pullulan, a polyvinyl pyrrolidone, polyacrylamide, a polyethylene glycol, a polypropylene glycol, etc. Preferably, it is polyvinyl alcohol.

[0060] Moreover, as a nonaqueous solubility high molecular compound, especially since distribution of a non-subtlety particle is stabilized, the nonaqueous solubility binder which dissolves in the mixed solvent of alcohols and these alcohols, such as ethanol and 2-propanol, and water is desirable. As such a nonaqueous solubility binder, acetal resin, such as vinyl pyrrolidone / vinyl acetate copolymer, a polyvinyl butyral, and a polyvinyl formal, can be mentioned, and since the degree of acetalization can make some water contain and can make distribution of a non-subtlety particle easy, especially the acetal resin of the range not more than 5 mol %20 mol % has it. [especially desirable]

[0061] These high molecular compounds may use independent thru/or plurality together, and add 2 - 30 % of the weight to a non-subtlety particle. Preferably, 5 - 20 % of the weight is added. Below in the range of the above-mentioned addition, paint film reinforcement becomes weak, and if many [too], ink absorptivity will fall.

[0062] In this invention, the lamination of an ink absorbing layer may be a monolayer, or may be a laminating configuration. In a laminating configuration, all layers may be layers of the same combination and you may be a laminating configuration with the layer which consists of other components.

[0063] The amount of coating of the ink absorbing layer containing the non-subtlety particle of this invention is 12g or more per unit square meter 60g or less preferably, in order 5g or more per unit square meter is required of solid content conversion and to accept the further effectiveness of this invention.

[0064] Furthermore, the non-subtlety particle of this invention and the coating liquid which forms the ink absorbing layer containing a binder if can add various well-known additives, such as a surface active agent, an inorganic pigment, a coloring color, a color pigment, an ink color fixing agent (cationic resin), an ultraviolet ray absorbent, an anti-oxidant, the dispersant of a pigment, a defoaming agent, a leveling agent, antiseptics, a fluorescent brightener, a viscosity stabilizer, pH regulator, and a hardening agent, if needed.

[0065] As a thermoplastic organic giant-molecule particle which can be used by this invention, these copolymers of ester of alpha [, such as polyolefines, such as the poly monochrome vinylidene aromatic series, such as polystyrene poly methyl styrene, poly methoxy styrene, and poly KURORU styrene, a polyvinyl chloride, a polyvinyl cyclohexane, polyethylene, polypropylene, and a polyvinylidene chloride, and the poly halo olefins polymethacrylate, poly KURORU acrylate and polymethylmethacrylate,] and beta-ethylene nature partial saturation acid, such as a polymer, etc. are mentioned, for example. Especially low consistency polyolefine can be used preferably.

[0066] A thermoplastic organic giant-molecule particle is obtained as the impalpable powder which ground the plastics of the plastics pigment and latex of the shape of a slurry which carried out emulsion polymerization, and which was built with a kind or the vinyl monomer beyond it, and its the shape of a dry matter or a solid-state with various means, powder cast microparticulate. As magnitude of a these thermoplasticity organic macromolecule particle, a thing with a diameter of 0.01 micrometers - 50 micrometers is usually used. A thing with a diameter of 0.1 micrometers - 20 micrometers is used preferably. It is not desirable, in order that the opening which will be formed if a diameter is smaller than 0.01 micrometers may become small too much and may make absorptivity of ink late. Moreover, if larger than 50 micrometers, since the particle which occupies a bigger area than the dot of ink will exist in a front face and image quality will deteriorate, it is not desirable.

[0067] The coating layer containing the thermoplastic organic macromolecule particle used for this invention can be made to contain colloidal silica. By blending colloidal silica within 30 weight sections to the thermoplastic organic macromolecule particle 100 weight section especially, since adhering to a heating roller is lost in case the adhesiveness of a thermoplastic organic macromolecule particle coat can be weakened and a heating coat is formed, it is desirable. When the 30 or more sections are added, the continuity of a coat is checked and the water resisting property of an image may be reduced.

[0068] As colloidal silica contained in the coating layer containing the thermoplastic organic macromolecule particle used by this invention, with a 5nm or more particle diameter [100nm or less] spherical colloidal silica, the un-spherical colloidal silica in which two or more these join together and have 30nm or more particle diameter of 800nm or less are mentioned, for example.

[0069] A high molecular compound may also be included in the coating layer containing the thermoplastic organic giant-molecule particle used for this invention as a binder. As a desirable high molecular compound, they are polyvinyl alcohol, acrylic resin, a styrene-acrylic copolymer, a maleic-anhydride polymer, a styrene maleic anhydride copolymer, an ethylene-vinylacetate copolymer, starch, polyvinyl pyridine, gelatin, casein, an ionomer, gum arabic, a carboxymethyl cellulose, an alginic acid, sodium alginate, a

pullulan, a polyvinyl pyrrolidone, polyacrylamide, a polyethylene glycol, a polypropylene glycol, etc., for example. Moreover, as a high molecular compound of nonaqueous solubility, they are latexes, such as polyacrylic ester, such as polyacetals, such as polyvinyl ester, such as polyvinyl acetate, and butyral resin, and polyacrylic acid ethyl, for example. Preferably, they are an ethylene-vinylacetate copolymer emulsion and a polyvinyl pyrrolidone. These high molecular compounds may use independent thru/or plurality together, and add 1 - 30 % of the weight to a thermoplastic organic macromolecule particle. Preferably, it is 3 - 20 % of the weight. The adhesive property of a thermoplastic organic macromolecule particle becomes a defect below in the range of the above-mentioned addition, and ink absorptivity is checked above the range of an addition.

[0070] As for the layer of the maximum surface which consists of a thermoplastic organic giant-molecule particle and a binder substantially, 0.5 g/m² - 50g/m² is desirable as an amount of coating (desiccation solid content). Furthermore, a pigment agent, thickener, fluid amelioration agent, defoaming agent, foam suppressor, release agent, foaming agent, penetrating agent, coloring color, color pigment, fluorescent brightener, ultraviolet ray absorbent, anti-oxidant, antiseptics, ** motorcycle agent, color fixing agent (cationic macromolecule), humid paper reinforcing agent, and desiccation paper reinforcing agent etc. can also be suitably blended as other additives.

[0071] When these ink absorbing layers and a thermoplastic organic macromolecule particle layer are prepared on said base material, the record medium which is excellent in the absorptivity of ink and a minute record image can record is obtained.

[0072] The various methods of application, such as E bar spreading, curtain spreading, SUTORADO hopper spreading, extrusion spreading, roll coating, air knife spreading, gravure spreading, and rod bar spreading, can be used for the approach of applying the coating liquid in this invention.

[0073] A general well-known approach can be used as a means to dry after coating, and it is not limited. for example, warming which ventilated the heating air generated according to the heat source -- it is the approach of making it passing near [, such as an approach, a heater, etc. which are conveyed in a vessel,] the heat source etc. As long as it can dry at the temperature which the thermoplastic macromolecule particle of the maximum surface does not fuse, what kind of approach may be used.

[0074] Moreover, after coating, you may finish using calenders, such as a machine calender, a supercalender, and a software calender.

[0075] The roles of the maximum surface which consist of a thermoplastic organic macromolecule particle in this invention are absorbing promptly the ink which flew and adhered to the maximum surface, and delivering a solvent to a lower layer, and becoming the layer which coat-izes and protects a record image from water or light with a suitable means after ink jet record.

[0076] The waterproof layer which carried out coating of the thermoplastics by the melting extrusion method is prepared in the opposite hand through a base material with the ink absorbing layer of this invention, and a thermoplastic organic macromolecule particle layer.

[0077] Polyolefin resin and polyester resin are mentioned as thermoplastics. As polyolefin resin, they are the copolymers which consist or more of two of olefins, such as a homopolymer of olefins, such as low density polyethylene, high density polyethylene,

polypropylene, polybutene, and the poly pentene, or ethylene propylene rubber, and such mixture. As polyester resin, they are polyethylene terephthalate, polybutylene terephthalate, polyethylenenaphthalate, etc. The thing of various kinds of consistencies and a melt viscosity characteristic (melt index) can be independently used for these thermoplastics for them, mixing. Preferably, they are polyethylene resin and polypropylene resin.

[0078] In this thermoplastics, moreover, white pigments, such as titanium oxide, a zinc oxide, talc, and a calcium carbonate, Fatty-acid amides, such as octadecanamide and an arachidic acid amide, zinc stearate, Fatty-acid metal salts, such as calcium stearate, aluminum stearate, and magnesium stearate, Blue pigments and colors, such as cobalt blue, ultramarine blue, sicilian blue, and a copper phthalocyanine blue, It can also add combining suitably various kinds of additives, such as a pigment of Magentas, such as cobalt violet, fast violet, and manganese purple, a color, a fluorescent brightener, an ultraviolet ray absorbent, and an antioxidant.

[0079] Before the waterproof layer prepared in the background of a base material in this invention is manufactured by the so-called extrusion coating method which casts the thermoplastics which carried out heating fusion, such as polyolefin resin and polyester resin, on the stencil it runs and covers resin in a stencil, it is desirable to perform activation, such as corona discharge treatment and flame treatment, to a covering surface. Although the front face of a waterproof layer is formed in a glossy surface, a mat side, etc. according to the front face of a cooling roll and it is not limited especially, the cooling roll of a fine split-face front face is used, and the front face which pressed down gloss a little is often used.

[0080] Moreover, before the coating of a waterproof layer prepares an ink absorbing layer and a thermoplastic organic macromolecule particle layer, coating of it may be carried out, but after carrying out coating of an ink absorbing layer or the thermoplastic organic macromolecule particle layer preferably, it is good to prepare a waterproof layer finally. The coating of the thermoplastic organic macromolecule particle layer may not be able to be carried out finely, but the reason is may be ruined, when a waterproof layer is in a base material beforehand. Although it is the translation which heating fusion is carried out, and a waterproof layer extrudes thermoplastics, and is prepared with a coating method, as for heating melting temperature, temperature high [around 300 degrees C] is usually used. Although the plasticization temperature of this thermoplastic organic macromolecule particle of a thermoplastic organic macromolecule particle layer established on the surface of the ink absorbing layer is 50 degrees C - about 150 degrees C, after preparing the layer, even if it paints the resin which carried out heating fusion on 300 degrees C and prepares a waterproof layer in the reverse side, a waterproof layer can be painted without influencing a thermoplastic organic macromolecule particle layer in any way. It will be for heat not to attain to even this thermoplastic organic macromolecule particle layer that is in an opposite hand through a paper base material, since heating melting resin is cooled by the cooling roll immediately after painting on paper.

[0081] Furthermore, on the waterproof layer, various kinds of exaggerated layers can be painted for antistatic nature, conveyance nature, curl tightness, note nature, sizing nature, etc. An exaggerated layer can be made to add combining suitably an inorganic antistatic agent, an organic antistatic agent, a hydrophilic binder, a latex, a curing agent, a pigment,

lubricant, a mat-ized agent, a surfactant, etc.

[0082] Since the thermoplastic organic macromolecule particle layer has the opening in the condition [that the ink jet record medium of this invention has recorded the alphabetic character and the image with the ink jet recording device], an image is whitish and is not so clear. After recording an ink jet record image, the process which it dissolves or dissolves, and the thermoplastic organic macromolecule particle of the maximum surface is coat-ized [process], and changes it to a waterproof transparent layer is required of this invention.

[0083] Give the solvent of a thermoplastic organic macromolecule, and it is made to dissolve as an approach of coat-izing the maximum surface, or there is the approach of applying and forming heat into a fusion coat etc. It is advantageous to coat formation to heat, after giving beforehand the matter which faces to apply heat and lowers the softening temperature of a thermoplastic organic macromolecule, especially a plasticizer.

[0084] Furthermore, it is desirable to give an ultraviolet ray absorbent which is usually used for a thermoplastic organic macromolecule, an antioxidant, a release agent, light stabilizer, etc. in order to prevent degradation of the formed thermoplastic organic macromolecule coat and to raise the lightfastness of the color of an ink jet image further.

[0085]

[Example] Although the example of this invention is given and explained below, this invention is not limited to these examples. Moreover, especially the "section" and "%" shown in an example, unless it shows clearly, weight section and weight % is shown.

[0086] To the mixed pulp which consists the needle-leaf tree bleaching kraft pulp which carried out beating of the broad-leaved tree bleaching kraft pulp which carried out beating to 320ml and csf by the <production of base material A> double disc refiner to 430ml and csf by 75 % of the weight and the double disc refiner of 25 % of the weight, 1.0 % of the weight of cation-ized starch, 0.1 % of the weight of alkyl ketene dimer sizing compounds, and a whiting loading material were added 7% of the weight, and the pulp slurry was prepared. From the pulp slurry, the web be formed with the Fortlinear paper machine, it dried at the multi-cylinder type dryer desiccation process after **** with a press, and the size press of the 5 - % of the weight solution of oxidized starch be carried out in the middle of desiccation (coating weight be 3.5 g/m² at double-sided desiccation solid content), machine calender processing be dry and carried out so that the base paper moisture obtain eventually might become 8% of the weight with bone dry moisture, and the base material A for the ink jet record media of basis weight 120 g/m² be manufactured.

[0087] To the side which prepares the ink absorbing layer of the <production of base material B> above-mentioned base material A, as white pigments, coating desiccation of the barium-sulfate (baryta) 100 section and the coating liquid which consists of the polyvinyl alcohol 10 section as adhesives was carried out so that it might be set to 10g/m² by desiccation solid content, and the base material B was manufactured.

[0088] 1200g [of <composition of hydrated alumina> ion exchange water] and isopropyl alcohol 900g was taught to the reactor of 3L, and it heated at 75 degrees C. Aluminum isopropoxide 408g was added, it performed by 75g and hydrolysis was performed at 95 degrees C of continuations for 10 hours for 24 hours. In addition, it agitated at 95 degrees C after hydrolysis for 48 hours 24g of acetic acids. Next, it condensed so that solid content concentration might become 15% of the weight, and the

dispersion liquid of white hydrated alumina were obtained. When this sol was dried at the room temperature and the X diffraction was measured, pseudo-boehmite structure was shown. Moreover, when mean particle diameter was measured with the transmission electron microscope, it was 30nm and was plate-like hydrated alumina of an aspect ratio 6.0. Moreover, when an average pore radius, pore volume, and a BET specific surface area were measured by the nitrogen adsorption desorption approach, they were 7.1nm, 0.65 ml/g, and 200m²/g, respectively.

[0089] <Ink absorbing layer coating liquid A> The 15 sections of 10% of the weight of polyvinyl alcohol (PVA235 by Kuraray Co., Ltd.) water solutions were mixed to the hydrated alumina dispersion-liquid 100 section using the dispersion liquid of 15% of the weight of the aforementioned hydrated alumina. It applied to the homomixer for 10 minutes by 10,000rpm after mixing, and homogeneity decentralization was carried out. The inspissation of the dispersion liquid was carried out by the evaporator so that it might become predetermined concentration, and they were used as coating liquid A.

[0090] The 15 sections of 10% of the weight of polyvinyl alcohol (PVA235 by Kuraray Co., Ltd.) water solutions were mixed to this alumina sol 100 section using the alumina sol 200 (Nissan Chemical Industries, Ltd. make) which is the <ink absorbing layer coating liquid B> amorphism alumina sol. It applied to the homomixer for 10 minutes by 10,000rpm after mixing, and homogeneity decentralization was carried out. The inspissation of the dispersion liquid was carried out by the evaporator so that it might become predetermined concentration, and they were used as coating liquid B.

[0091] As a <ink absorbing layer coating liquid C> alumina particle, the agitator distributed Aerosil aluminum oxide C(product made from Japanese Aerosil) of 13nm of diameters of primary particle which are delta group's gamma mold alumina crystal powder600g in 2400g ion exchange water, and the viscous liquid of the shape of 20% of the weight of a slurry was prepared. The 30 sections of 10% of the weight of polyvinyl alcohol (PVA235 by Kuraray Co., Ltd.) water solutions were mixed to the alumina dispersion-liquid 100 section using 20% of the weight of these gamma mold alumina dispersion liquid. It applied to the homomixer for 10 minutes by 10,000rpm after mixing, and homogeneity decentralization was carried out. The inspissation of the dispersion liquid was carried out by the evaporator so that it might become predetermined concentration, and they were used as coating liquid C.

[0092] The application constituent of the <ink absorbing layer coating liquid D> ink absorbing layer distributed gaseous-phase method particle silica (AEROSIL300: product made from Japanese Aerosil) of 7nm of diameters of primary particle 100g with the agitator in 500g ion exchange water, mixed 80g and used 10% of the weight of the polyvinyl alcohol (PVA235 by Kuraray Co., Ltd.) water solution as coating liquid D.

[0093] As commercial spherical colloidal silica, the application constituent of the <ink absorbing layer coating liquid E> ink absorbing layer mixed the Snow tex O(Nissan Chemical Industries, Ltd. make, primary particle diameter [of 10-20nm], SiO₂ concentration 20 - 21 % of the weight)200 section, 10% of the weight of the polyvinyl alcohol (PVA117 by Kuraray Co., Ltd.) 30 section, and the cationic color fixing agent (Sumi Reds resin 1001: Sumitomo Chemical Co., Ltd. make) 20 section, and used them as coating liquid E.

[0094] As commercial un-spherical colloidal silica, the application constituent of the <ink absorbing layer coating liquid F> ink absorbing layer mixed the Snow tex UP(Nissan

Chemical Industries, Ltd. make, primary particle diameter [of 10-20nm], secondary [an average of] particle diameter [of about 70nm], SiO₂ concentration 20 - 21 % of the weight) 200 section, 10% of the weight of the polyvinyl alcohol (PVA117 by Kuraray Co., Ltd.) 30 section, and the cationic color fixing agent (Sumi Reds resin 1001: Sumitomo Chemical Co., Ltd. make) 20 section, and used them as coating liquid F. [0095] The application constituent of the <ink absorbing layer coating liquid G> ink absorbing layer mixed the primary particle diameter of about 10-30nm, the second [an average of] particle diameter of 3.7 micrometers, the synthetic amorphous silica (fine seal X-37B: Tokuyama make) 100 section of 270m²/[of BET specific surface areas] g, the polyvinyl alcohol (PVA117: Kuraray Co., Ltd. make) 30 section, and the cationic color fixing agent (Sumi Reds resin 1001: Sumitomo Chemical Co., Ltd. make) 20 section, and used them as coating liquid G.

[0096]

The <thermoplastic organic macromolecule particle content layer combination A> thermoplasticity organic macromolecule particle (CHEMIPEARL M200: Mitsui Chemicals, Inc. make) The 25 sections (solid content)

Polyvinyl pyrrolidone The 3.0 sections [0097]

The <thermoplastic organic macromolecule particle content layer combination B> thermoplasticity organic macromolecule particle (CHEMIPEARL M200: Mitsui Chemicals, Inc. make) The 25 sections (solid content)

Colloidal silica (the Snow tex O, the Nissan chemistry company make) 7 section polyvinyl pyrrolidone The 3.0 sections [0098] it becomes amount of desiccation coating 15 g/m² to the example 1 base material A by the curtain coating machine about the coating liquid of the ink absorbing layer combination A -- as -- coating -- it dries and becomes amount of desiccation coating 10 g/m² by curtain coater on it about the coating liquid of the thermoplastic organic macromolecule particle content layer combination A - - as -- coating -- it dried. Subsequently, the high-density-polyethylene resin of 3 was fused at 320 degrees C the consistency of 0.962g/cm, extrusion coating was carried out so that it might become 30 micrometers in thickness in the field in which the ink absorbing layer of a base material is not established, the rear-face resin coat of 5% of glossiness was carried out using the split-face cooling roll, the waterproof layer was created, and the ink jet record medium of an example 1 was produced.

[0099] it becomes amount of desiccation coating 15 g/m² to the example 2 base material A by the curtain coating machine about the coating liquid of the ink absorbing layer combination A -- as -- coating -- it dries and becomes amount of desiccation coating 10 g/m² by curtain coater on it about the coating liquid of the thermoplastic organic macromolecule particle content layer combination B -- as -- coating -- it dried. Subsequently, the high-density-polyethylene resin of 3 was fused at 320 degrees C the consistency of 0.962g/cm, extrusion coating was carried out so that it might become 30 micrometers in thickness in the field in which the ink absorbing layer of a base material is not established, the rear-face resin coat of 5% of glossiness was carried out using the split-face cooling roll, the waterproof layer was created, and the ink jet record medium of an example 2 was produced.

[0100] In example 3 example 1, changed to the ink absorbing layer combination A, and the ink absorbing layer combination B was used, and also the ink jet record medium of an example 3 was produced like the example 1.

[0101] In example 4 example 2, changed to the ink absorbing layer combination A, and the ink absorbing layer combination B was used, and also the ink jet record medium of an example 4 was produced like the example 2.

[0102] In example 5 example 1, changed to the ink absorbing layer combination A, and the ink absorbing layer combination C was used, and also the ink jet record medium of an example 5 was produced like the example 1.

[0103] In example 6 example 2, changed to the ink absorbing layer combination A, and the ink absorbing layer combination C was used, and also the ink jet record medium of an example 6 was produced like the example 2.

[0104] In example 7 example 1, changed to the ink absorbing layer combination A, and the ink absorbing layer combination D was used, and also the ink jet record medium of an example 7 was produced like the example 1.

[0105] In example 8 example 2, changed to the ink absorbing layer combination A, and the ink absorbing layer combination D was used, and also the ink jet record medium of an example 8 was produced like the example 2.

[0106] In example 9 example 1, changed to the ink absorbing layer combination A, and the ink absorbing layer combination E was used, and also the ink jet record medium of an example 9 was produced like the example 1.

[0107] In example 10 example 2, changed to the ink absorbing layer combination A, and the ink absorbing layer combination E was used, and also the ink jet record medium of an example 10 was produced like the example 2.

[0108] In example 11 example 1, changed to the ink absorbing layer combination A, and the ink absorbing layer combination F was used, and also the ink jet record medium of an example 11 was produced like the example 1.

[0109] In example 12 example 2, changed to the ink absorbing layer combination A, and the ink absorbing layer combination F was used, and also the ink jet record medium of an example 12 was produced like the example 2.

[0110] In example 13 example 1, changed to the ink absorbing layer combination A, and the ink absorbing layer combination G was used, and also the ink jet record medium of an example 13 was produced like the example 1.

[0111] In example 14 example 2, changed to the ink absorbing layer combination A, and the ink absorbing layer combination G was used, and also the ink jet record medium of an example 14 was produced like the example 2.

[0112] it becomes amount of desiccation coating 15 g/m² to the side which prepared the baryta coating layer of the example 15 base material B by the curtain coating machine about the coating liquid of the ink absorbing layer combination A -- as -- coating -- it dries and becomes amount of desiccation coating 10 g/m² by curtain coater on it about the coating liquid of the thermoplastic organic macromolecule particle content layer combination A -- as -- coating -- it dried. Subsequently, the high-density-polyethylene resin of 3 was fused at 320 degrees C the consistency of 0.962g/cm, extrusion coating was carried out so that it might become 30 micrometers in thickness in the field in which the ink absorbing layer of a base material is not established, the rear-face resin coat of 5% of glossiness was carried out using the split-face cooling roll, the waterproof layer was created, and the ink jet record medium of an example 15 was produced.

[0113] it becomes amount of desiccation coating 15 g/m² to the side which prepared the baryta coating layer of the example 16 base material B by the curtain coating machine

about the coating liquid of the ink absorbing layer combination A -- as -- coating -- it dries and becomes amount of desiccation coating 10 g/m² by curtain coater on it about the coating liquid of the thermoplastic organic macromolecule particle content layer combination B -- as -- coating -- it dried. Subsequently, the high-density-polyethylene resin of 3 was fused at 320 degrees C the consistency of 0.962g/cm, extrusion coating was carried out so that it might become 30 micrometers in thickness in the field in which the ink absorbing layer of a base material is not established, the rear-face resin coat of 5% of glossiness was carried out using the split-face cooling roll, the waterproof layer was created, and the ink jet record medium of an example 16 was produced.

[0114] In example 17 example 15, changed to the ink absorbing layer combination A, and the ink absorbing layer combination B was used, and also the ink jet record medium of an example 17 was produced like the example 15.

[0115] In example 18 example 16, changed to the ink absorbing layer combination A, and the ink absorbing layer combination B was used, and also the ink jet record medium of an example 18 was produced like the example 16.

[0116] In example 19 example 15, changed to the ink absorbing layer combination A, and the ink absorbing layer combination C was used, and also the ink jet record medium of an example 19 was produced like the example 15.

[0117] In example 20 example 16, changed to the ink absorbing layer combination A, and the ink absorbing layer combination C was used, and also the ink jet record medium of an example 20 was produced like the example 16.

[0118] In example 21 example 15, changed to the ink absorbing layer combination A, and the ink absorbing layer combination D was used, and also the ink jet record medium of an example 21 was produced like the example 15.

[0119] In example 22 example 16, changed to the ink absorbing layer combination A, and the ink absorbing layer combination D was used, and also the ink jet record medium of an example 22 was produced like the example 16.

[0120] In example 23 example 15, changed to the ink absorbing layer combination A, and the ink absorbing layer combination E was used, and also the ink jet record medium of an example 23 was produced like the example 15.

[0121] In example 24 example 16, changed to the ink absorbing layer combination A, and the ink absorbing layer combination E was used, and also the ink jet record medium of an example 24 was produced like the example 16.

[0122] In example 25 example 15, changed to the ink absorbing layer combination A, and the ink absorbing layer combination F was used, and also the ink jet record medium of an example 25 was produced like the example 15.

[0123] In example 26 example 16, changed to the ink absorbing layer combination A, and the ink absorbing layer combination F was used, and also the ink jet record medium of an example 26 was produced like the example 16.

[0124] In example 27 example 15, changed to the ink absorbing layer combination A, and the ink absorbing layer combination G was used, and also the ink jet record medium of an example 27 was produced like the example 15.

[0125] In example 28 example 16, changed to the ink absorbing layer combination A, and the ink absorbing layer combination G was used, and also the ink jet record medium of an example 28 was produced like the example 16.

[0126] In example of comparison 1 example 1, a waterproof layer on the back was not

prepared, and also the ink jet record medium of the example 1 of a comparison was produced like the example 1.

[0127] In example of comparison 2 example 15, a waterproof layer on the back was not prepared, and also the ink jet record medium of the example 2 of a comparison was produced like the example 15.

[0128] In example of comparison 3 example 1, it changed to the waterproof layer on the back, and using the air knife coater, coating desiccation of the application constituent which adjusted and obtained the 1st class kaolin 50 commercial section, the styrene-butadiene system latex 50 commercial section, and the oxidized starch 5 commercial section at 50% of solid content concentration was carried out so that it might be set to the amount of desiccation coating of 15g/m², and also the ink jet record medium of the example 3 of a comparison was produced like the example 1.

[0129] The Epson color ink jet printer (PM-770C) was used for the ink jet record medium obtained by the <production of ink jet record object> above, poor printing of four primary colors and record of a high definition photograph were performed, subsequently to 120 degrees C, it heated, and the maximum surface was fused and coat-ized. Thus, the following assessment approach estimates, the result is summarized, and the produced ink jet record object is shown in a table 1.

[0130] <Ink absorptivity> The overflow of the ink of the part which drew the high definition photograph, and the thing which evaluates blot condition by viewing, does not bear an outstanding thing at O, and does not bear a general thing at ** and an activity were made into x.

[0131] O and the thing to which it is somber and it seems that the haze started a little were made into **, and the image quality of a <image color nature> record image made [that the image after coat-izing the maximum surface appears clear thoroughly] x that to which saturation is falling whitely for O and the thing which looks clear. O The above is good as color nature.

[0132] the stream after a <image water resisting property> image water resisting property coat-izes the maximum surface -- it exposed to inside for 1 hour, and O and an image spread a little that to which an image spread or did not flow at all, ** and an image spread the blurred thing, or it faded and flowed, and the thing was made into x. O The thing of a water resisting property is good.

[0133]

[A table 1]

試料No.	吸 収 性	色 彩 性	耐 水 性	試料No.	吸 収 性	色 彩 性	耐 水 性
実施例 1	◎	○	○	実施例 15	◎	○	○
実施例 2	○	◎	○	実施例 16	○	◎	○
実施例 3	◎	○	○	実施例 17	◎	○	○
実施例 4	○	◎	○	実施例 18	○	◎	○
実施例 5	◎	○	○	実施例 19	◎	○	○
実施例 6	○	◎	○	実施例 20	○	◎	○
実施例 7	◎	○	○	実施例 21	◎	○	○
実施例 8	○	◎	○	実施例 22	○	◎	○
実施例 9	◎	○	○	実施例 23	◎	○	○
実施例 10	○	◎	○	実施例 24	○	◎	○
実施例 11	◎	○	○	実施例 25	◎	○	○
実施例 12	○	◎	○	実施例 26	○	◎	○
実施例 13	◎	○	○	実施例 27	◎	○	○
実施例 14	○	◎	○	実施例 28	○	◎	○
比較例 1	◎	○	×				
比較例 2	○	◎	×				
比較例 3	○	○	△				

[0134] From the result of a table 1, like the example of this invention, in an ink absorbing layer lower layer Colloidal silica, A gaseous-phase method silica, hydrated alumina, and gamma mold aluminum-oxide particle are contained. To the ink jet record medium which prepared the thermoplastic organic macromolecule particle layer in the upper layer, and prepared the waterproof layer by the melting extrusion method of thermoplastics in the field of the opposite hand further, after image recording, Although the examples 1 and 2 of a comparison which have not prepared the waterproof layer although color nature, absorptivity, and the water resisting property of the record object to which heat was applied, and which coat-ized the thermoplastic organic macromolecule particle layer with heat are altogether good were inferior with the water resisting property and the example 3 of a comparison prepared the resin layer by the melting extrusion method further, a water resisting property is not bad practical too.

[0135]

[Effect of the Invention] As mentioned above, according to this invention, since a front face is covered by carrying out printing afterbaking by melting resin and the effect by osmosis of the water from a background is moreover also eliminated, a waterproof good ink jet record object is obtained extremely, and the ink jet record medium which was further excellent also in color nature and ink absorptivity is obtained.